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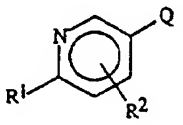
(54) Title: ARTHROPODICIDAL AZACYCLIC HETEROCYCLES



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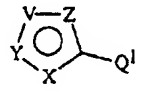

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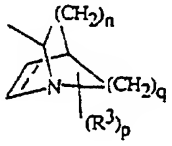
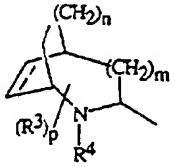


Q-1



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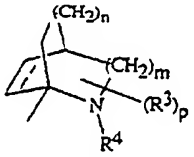

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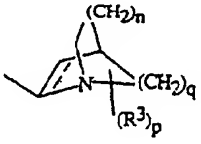
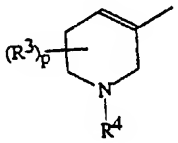
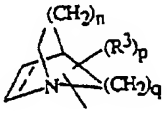


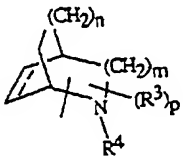
Q-4



Q-5



Q-6



Q-7

(57) Abstract

Arthropodicidal compounds having formula (I) and compositions comprising compounds of formula (II) and use of said compounds to control arthropods, wherein Q is selected from the group Q-1, Q-2, Q-3 and Q-4; and Q^1 is selected from the group Q-5, Q-6 and Q-7.

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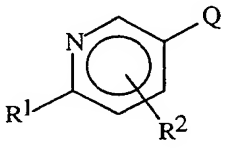
ARTHROPODICIDAL AZACYCLIC HETEROCYCLES

The present invention comprises compounds useful for the control of arthropods. EP 412,798 A2 discloses pyridinyl-substituted azabicyclic compounds for use in dementia provided the pyridinyl ring is not attached to the 2'-carbon position of the azabicyclic moiety. *J. Gen. Chem. U.S.S.R.*, (1963), 33, 3345 discloses 2-(3-pyridinyl)-1-azabicyclo[2.2.2]octane, however, no utility is taught. WO 93/14636 discloses azacyclic rings substituted with an optionally substituted oxadiazolyl or thiadiazolyl ring as insecticides. None of these references specifically teaches the compounds of the present invention.

SUMMARY OF THE INVENTION

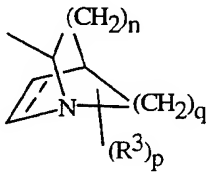
This invention pertains to compounds of Formula I, including all geometric and stereoisomers and agriculturally suitable salts thereof. The compounds are:



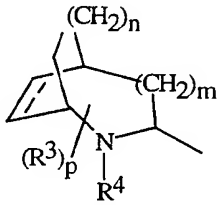
I

wherein:

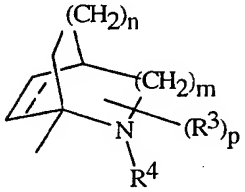
Q is selected from the group



Q-1

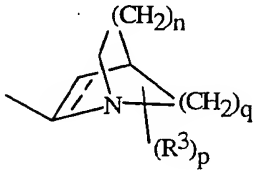


Q-2



Q-3

and



Q-4 ;

where the broken line represents an optional chemical bond;

R^1 and R^2 are independently selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^5)R^6$, OR^5, $C(O)R^5$, $C(O)OR^5$, $C(O)N(R^5)R^6$, SR^5, $S(O)R^5$, $S(O)_2R^5$, $S(O)_2N(R^5)R^6$ and C_1-C_6 alkyl substituted with 1 or 2 groups

independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl; R^2 being attached to any unsubstituted aromatic ring carbon; and R^1 and R^2 are not both hydrogen when Q is Q-1 or Q-4, n is 1, R^3 is H and q is 2;

R^3, which is attached to any carbon of the azabicyclic ring including the carbon directly attached to the heterocyclic aromatic ring, is selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^7)R^8$, OR^7, $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7, $S(O)R^7$, $S(O)_2R^7$, $S(O)_2N(R^7)R^8$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from the group NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^4 is selected from the group H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, $N(R^9)R^{10}$, $C(O)R^9$, $C(O)OR^9$, $C(O)N(R^9)R^{10}$, SR^9, $S(O)R^9$, $S(O)_2R^9$, $S(O)_2N(R^9)R^{10}$, benzyl and $CH(CH_3)Ph$; provided when any of R^1, R^2, R^3 or R^4 is $S(O)R^5$, $S(O)_2R^5$, $S(O)R^7$, $S(O)_2R^7$, $S(O)R^9$, or $S(O)_2R^9$ then R^5, R^7 and R^9 are other than H;

R^5, R^6, R^7,R^8, R^9 and R^{10} are independently selected the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from W, and benzyl optionally substituted with 1 or 2 substitutents independently selected from W;

W is selected from the group halogen, NO_2, CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

m and n are independently 0, 1 or 2;

p is 1 or 2; and

q is 1, 2 or 3.

Preferred Compounds A are compounds of Formula I wherein Q is Q-1.

Preferred Compounds B are compounds of Preferred A wherein:

R^1 is selected from the group H, halogen and C_1-C_2 alkyl;

R^2 is selected from the group H and Cl;

R^3 is selected from the group H, halogen, C_1-C_6 alkyl and OR^7;

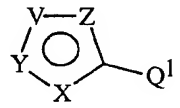
R^5 is selected from the group H and C_1-C_4 alkyl ; and

n is 0 or 1.

Specifically preferred for biological activity is Compound C of Preferred B which is:

7-(6-chloro-3-pyridinyl)-1-azabicyclo[2.2.1]heptane.

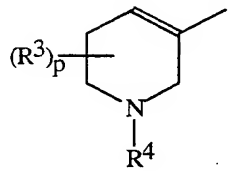
This invention also includes arthropodicidal compositions and method of use in both agronomic and nonagronomic environments wherein the arthropodicidal compounds are those of the formula:



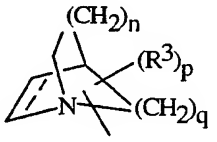
II

wherein:

Q^1 is selected from the group

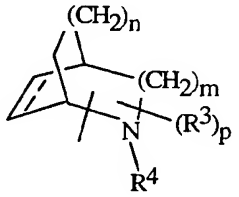


Q-5



Q-6

and



Q-7

;

where the broken line represents an optional chemical bond;

V, X, Y and Z of the ring are each independently selected from the group O, S, N, $-C(R^1)-$, $-C(R^1)=C(R^2)-$, $-C(R^1)=N-$ and $-N(R^{11})-$; provided that (i) no more than one of V, X, Y or Z is $-C(R^1)=C(R^2)-$, $-C(R^1)=N-$, $-N(R^{11})-$, O or S, (ii) at least one of V, X, Y or Z is N, (iii) when the ring is a 5-membered ring containing two N and one O or S, and Q is Q-6, then the ring is attached to the 2-position of Q^1 and (iv) when the ring is a 5-membered ring containing two N and one O or S, then Q is other than Q-5;

R^1 and R^2 are independently selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^5)R^6$, OR^5, $C(O)R^5$, $C(O)OR^5$, $C(O)N(R^5)R^6$, SR^5, $S(O)R^5$, $S(O)_2R^5$, $S(O)_2N(R^5)R^6$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from the group NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^3, which is attached to any carbon of the azacyclic ring including the carbon directly attached to the heterocyclic aromatic ring, is selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^7)R^8$, OR^7, $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7, $S(O)R^7$, $S(O)_2R^7$, $S(O)_2N(R^7)R^8$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^4 and R^{11} are independently selected from the group H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, $N(R^9)R^{10}$, $C(O)R^9$, $C(O)OR^9$, $C(O)N(R^9)R^{10}$, SR^9, $S(O)R^9$, $S(O)_2R^9$, $S(O)_2N(R^9)R^{10}$, benzyl and $CH(CH_3)Ph$; provided when any of R^1, R^2, R^3 or R^4 is $S(O)R^5$, $S(O)_2R^5$, $S(O)R^7$, $S(O)_2R^7$, $S(O)R^9$, or $S(O)_2R^9$ then R^5, R^7 and R^9 are other than H;

R^5, R^6, R^7,R^8, R^9 and R^{10} are independently selected the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from W, and benzyl optionally substituted with 1 or 2 substitutents independently selected from W;

W is selected from the group halogen, NO_2, CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

m and n are independently 0, 1 or 2;

p is 1 or 2; and

q is 1, 2 or 3.

Preferred Method A is the method wherein:

R^1 is selected from the group H, halogen and C_1-C_2 alkyl;

R^2 is selected from the group H and Cl;

R^3 is selected from the group H, halogen, C_1-C_6 alkyl and OR^7;

R^5 is selected from the group H and C_1-C_4 alkyl; and

m and n are 0 or 1.

Preferred Method B is the method of Preferred A wherein:

V is N;

X is $-C(R^1)=C(R^2)-$;

Y and Z are $-C(R^1)-$; and

Q^1 is Q-6.

Preferred Method C is the method of Preferred A wherein:

V is N;

X is S;

Y and Z are -C(R^1)-; and

Q^1 is Q-6.

Preferred Method D is the method of Preferred A wherein:

the ring contains two N and one O or S; and

Q^1 is Q-6.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active than the others and how to separate stereoisomers. Accordingly, the present invention comprises racemic and optically active compound(s) of Formulae I and II as well as agriculturally suitable salts thereof. The term optically active compound(s) includes individual stereoisomers, mixtures of stereoisomers enriched in one stereoisomer, and optically active mixtures of compounds.

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" denotes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. "Alkenyl" denotes straight-chain or branched alkenes such as ethenyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also denotes polyenes such as 1,3-hexadiene. "Alkynyl" denotes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 3-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also denote moieties comprised of multiple triple bonds such as 2,4-hexadiyne. "Alkoxy" denotes methoxy, ethoxy, *n*-propyloxy and isopropyloxy isomers. "Cycloalkyl" denotes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C, $ClCH_2$, CF_3CH_2 and CF_3CCl_2. Examples of "haloalkenyl" include $(Cl)_2C{=}CHCH_2$ and $CF_3CH_2CH{=}CHCH_2$. Examples of "haloalkynyl" include $HC{\equiv}CCHCl$, $CF_3C{\equiv}C$, $CCl_3C{\equiv}C$ and $FCH_2C{\equiv}CCH_2$. The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 6. For example, C_1-C_3 alkyl designates methyl through propyl; C_2 alkoxy designates CH_3CH_2O; C_3 alkoxy designates $CH_3CH_2CH_2O$ or $(CH_3)_2CHO$.

Examples of "alkoxycarbonyl" include $CH_3OC(=O)$, $CH_3CH_2OC(=O)$, $CH_3CH_2CH_2OC(=O)$ and $(CH_3)_2CHOC(=O)$.

Examples of Formula II heterocyclic rings, exclusive of Q^1, include pyrrolyl, imidazolyl, pyrazolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, oxazinyl, thiazinyl, oxadiazinyl, thiadiazinyl, triazinyl and tetrazinyl.

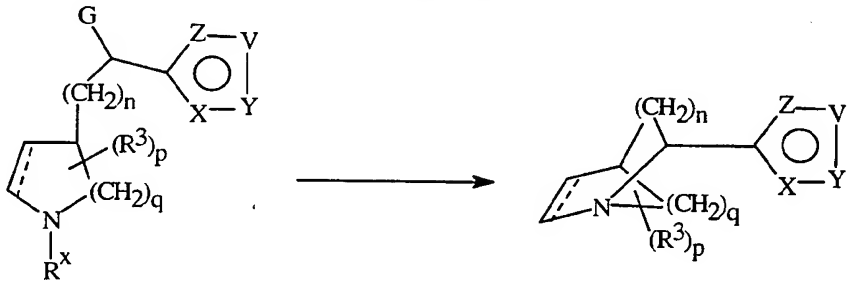
The 2-position of the azabicyclic ring is defined as any carbon atom directly attached to the nitrogen atom of the azabicyclic ring. The 3-position is defined as any carbon atom directly attached to any carbon atom which is directly attached to the nitrogen atom of the azabicyclic ring.

When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can exceed 1, said substituents (when they exceed 1) are independently selected from the group of defined substituents. Similarly, when a compound is substituted with a substituent which occurs more than once, said substituent is independently selected from the group defined for said substituent.

DETAILS OF THE INVENTION

Compounds of Formula I (Q-1) and Formula II (Q-6) can be prepared by intramolecular alkylation of amino compounds of Formula III where G is a suitable leaving group such as a halogen or sulfonate. The reaction can be performed in the absence or presence of a base in a suitable solvent. Suitable solvents include tetrahydrofuran, diethyl ether and dimethoxyethane. Examples of typical bases include sodium methoxide, potassium *t*-butoxide and sodium hydride. The reactions can be run at temperatures in the range of 25°C to reflux. This method is similar to procedures described in the art (*Chimia* (1976) *30*, 60). Scheme I illustrates this reaction.

Scheme I

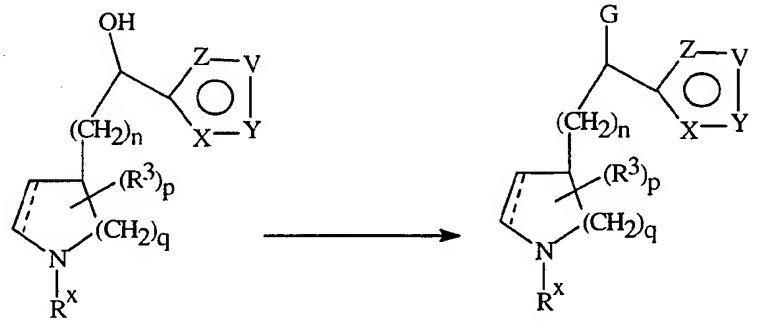


III (where $R^X = H$) I (Q-1) and II (Q-6)

Compounds of Formula III can be prepared by reaction of the hydroxy compounds of Formula IV with a halogenating agent such as thionyl chloride, phosphorous tribromide or a sulfonylating agent such as methanesulfonyl chloride or *p*-toluenesulfonyl chloride using procedures that are known to one skilled in the art

(March, J. *Advanced Organic Chemistry*, John Wiley & Sons, New York, 3rd ed. (1985) 1151). Scheme II illustrates this transformation.

Scheme II



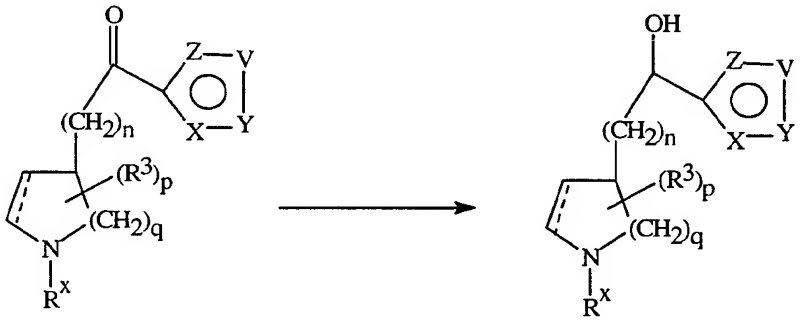
IV (where $R^X = H$)

III (where $R^X = H$)

G is halogen or sulfonate

Formula IV compounds can be prepared by reduction of ketones with a reducing agent such as sodium borohydride, borane, and lithium aluminum hydride using procedures that are known to one skilled in the art (March, J. *Advanced Organic Chemistry*, John Wiley & Sons, New York, 3rd ed. (1985) 1147). Scheme III illustrates this transformation.

Scheme III

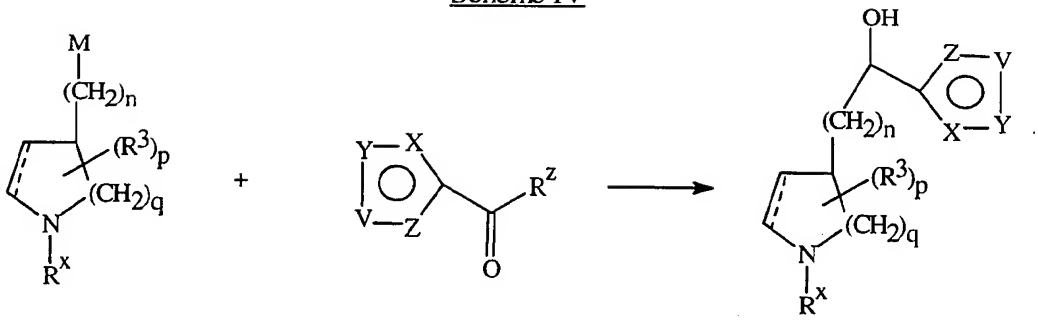


V (where $R^X = H$)

IV (where $R^X = H$)

Alternatively, Formula IV compounds can be prepared by addition of an appropriate organometallic compound VI (where M = Li, Mg, Cu, Zn) to a carbonyl compound VII in a suitable solvent such as diethyl ether, tetrahydrofuran and dimethoxyethane. The reaction can be run at temperatures from -78°C to 35°C. Scheme IV illustrates this transformation.

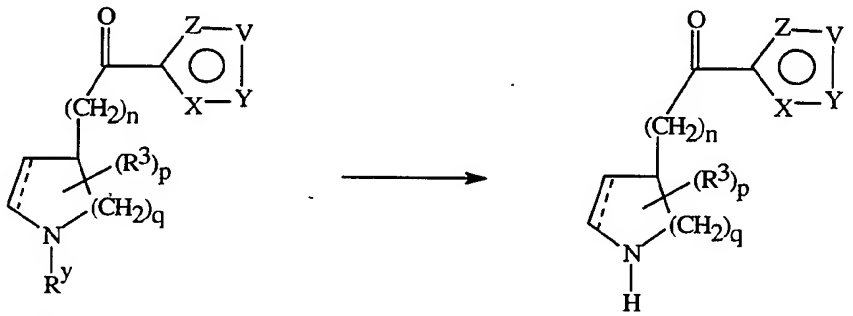
Scheme IV



VI (where $R^X \neq H$) VII ($R^Z = H$) IV (where $R^X \neq H$)

Compounds of Formula V can be prepared by deprotection of compounds of Formula VIII using procedures known to one skilled in the art (Greene, *Protective Groups in Organic Synthesis*, 2nd ed. (1991) 315-348). Scheme V illustrates this transformation.

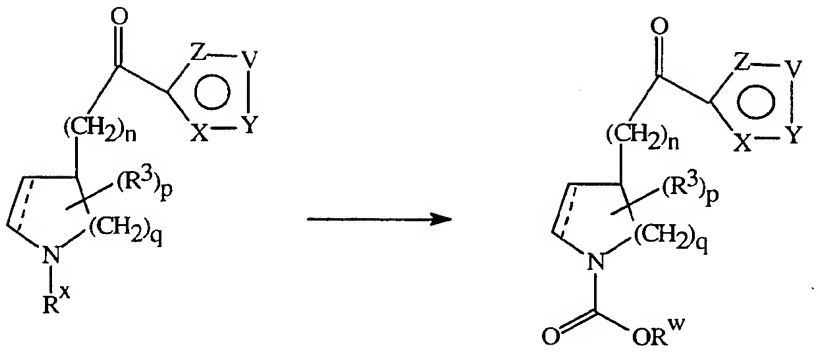
Scheme V



VIII (R^y is a protecting group) V

Compounds of Formula VIII can be prepared by de-alkylation of Formula IX compounds with a chloroformate derivative such as 1-chloroethyl chloroformate, benzyl chloroformate, and 2,2,2-trichloroethyl chloroformate in a suitable solvent such as methylene chloride, chloroform, and 1,2-dichloroethane. The reactions are usually run at temperatures in the range of 25°C to the reflux temperature of the particular solvent. Scheme VI illustrates this transformation.

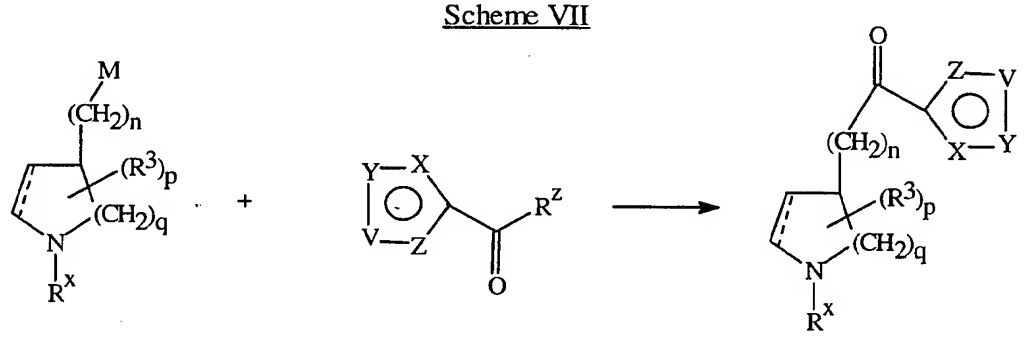
Scheme VI



IX (where $R^X = C_1$-C_6 alkyl, benzyl) VIII (R^W = alkyl, haloalkyl)

Compounds of Formula IX can be prepared by addition of an organometallic compound of Formula VI to carbonyl compounds of Formula VII in an analogous procedure described for Formula IV compounds. Scheme VII illustrates this transformation.

Scheme VII

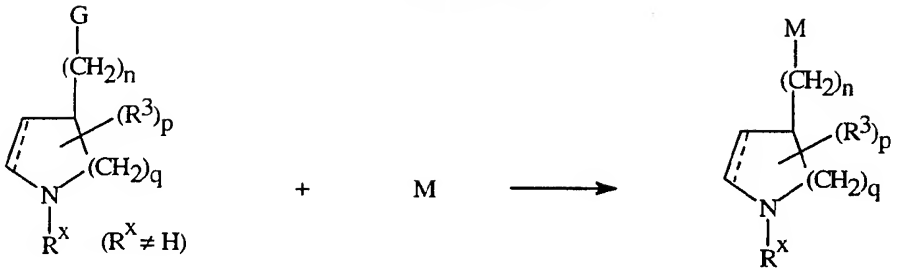


VI (where R^X = H) VII (where R^Z = Cl, N(OMe)Me, alkoxy) IX

Carbonyl compounds of Formula VII where R^Z is -N(OMe)Me can be prepared from carboxylic acid derivatives using procedures known in the art (*Org. Prep. Proc.* (1993) *25*, 15).

Organometallic compounds of Formula VI can be prepared by reaction of Formula X with a reactive metal species, such as magnesium, using procedures similar to those described in the art (*J. Med. Chem.* (1965) *8*, 829). One skilled in the art will recognize this as a Grignard reagent. Alternatively, Formula VI compounds (M=Li) can be obtained by lithium/halogen exchange using procedures known to one skilled in the art (March, J. *Advanced Organic Chemistry*, John Wiley & Sons, New York, 3rd ed. (1985) 1169).

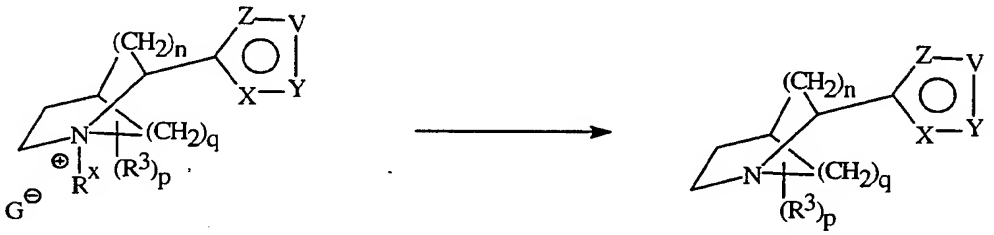
Scheme VIII



X (G= halogen) (M is magnesium or lithium reagent) VI (M is Mg or Li)

Alternatively, compounds of Formula I (Q-1) and Formula II (Q-6) can be prepared by deprotection of salts of Formula XI by hydrogenation in the presence of a suitable catalyst and solvent. Suitable catalysts include palladium on carbon and platinum oxide. Appropriate solvents are methanol, ethanol and ethyl acetate. Similar procedures are described in the art (*J. Chem. Soc., Perkin Trans. I*, (1991) 1091). Scheme IX illustrates this transformation.

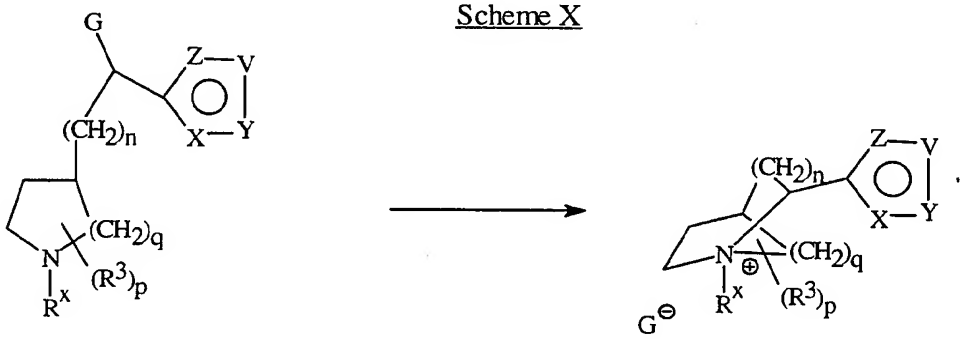
Scheme IX



XI (where R^X = benzyl, G is halogen or sulfonate) I (Q-1) and II (Q-6)

Salts of Formula XI can be prepared by cyclization of Formula III compounds in a suitable solvent. Suitable solvents are ethanol, 1,2-dichloroethane and toluene. The reaction can be run at temperatures in the range of 0°C to reflux. Scheme X illustrates this reaction.

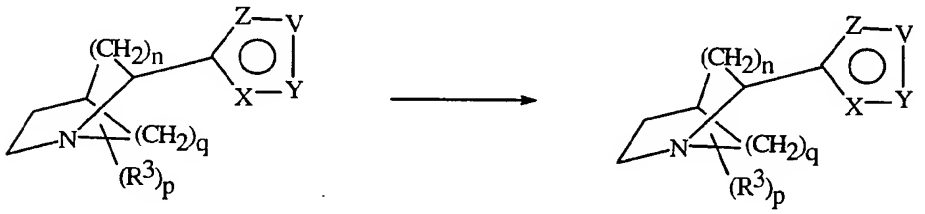
Scheme X



III (where R^X = C_1-C_6 alkyl, benzyl, G is halogen or sulfonate) XI

One skilled in the art will recognize that one substituent can be converted into another. For example, compound I (V=CR^1, R^1=Cl) can be converted into I (V=CR^1, R^1=OMe) by displacement with methoxide, or converted into I (V=CR^1, R^1=alkyl) by reaction with an organostannane under palladium catalysis. Scheme XI illustrates this transformation.

Scheme XI

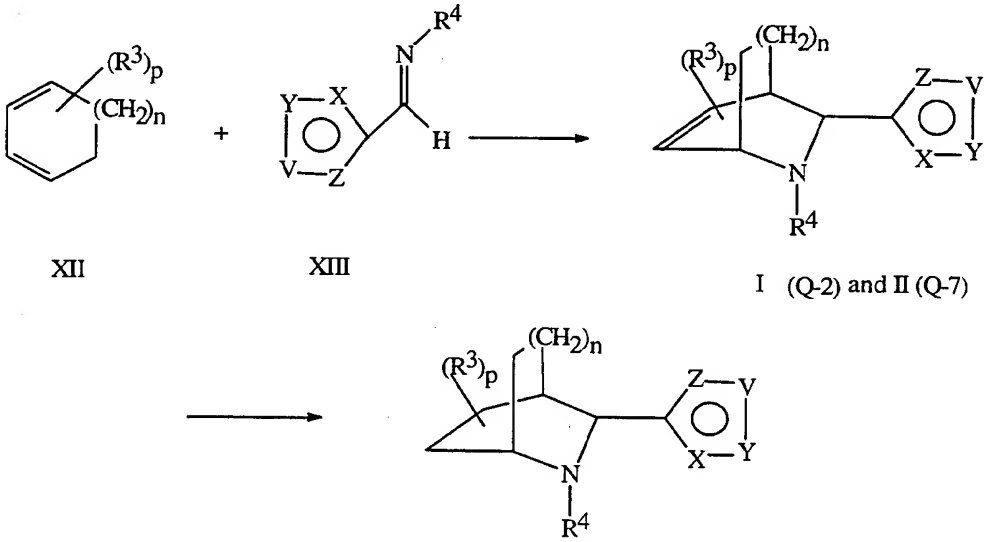


I (where V=CR^1, R^1 = halogen)

I (where V=CR^1, R^1 = alkyl, alkoxy, thioalkyl, alkenyl, etc.)

Compounds of Formula I (Q-2) and Formula II (Q-7) can be prepared by cycloaddition of compounds of Formula XII with imines of Formula XIII. The reaction can be performed in the absence or presence of an acid such as zinc chloride, boron trifluoride, and hydrogen chloride. Suitable solvents are dichloromethane, toluene, tetrahydrofuran, and water. The reactions can be run at temperatures ranging from -78°C to reflux temperature of the solvent. It will be recognized by those skilled in the art that fully saturated azabicyclic analogs can be prepared by simple reduction of the olefin. Scheme XII illustrates this transformation.

Scheme XII



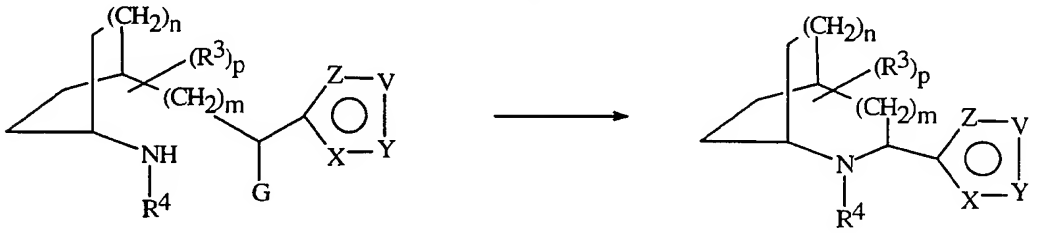
XII XIII

I (Q-2) and II (Q-7)

I (Q-2) and II (Q-7)

Alternatively, compounds of Formula I (Q-2) and Formula II (Q-7) can be prepared by intramolecular alkylation of Formula XIV compounds in a similar fashion to methods described for Formula I (Q-1) compounds. Scheme XIII illustrates this transformation.

Scheme XIII



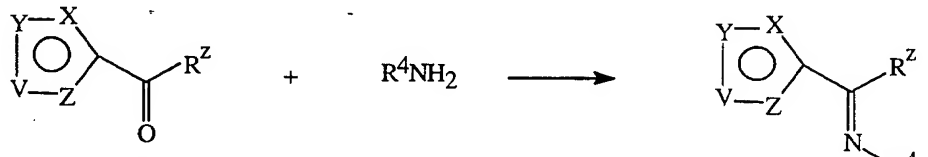
XIV

G is halogen or sulfonate

I (Q-2) and II (Q-7)

Imines of Formula XIII can be prepared by condensation of Formula VII carbonyl compounds with a primary amine (R^4NH_2) using procedures known to one skilled in the art (March, J. *Advanced Organic Chemistry*; John Wiley & Sons, New York, 3rd ed. (1985) 465). Scheme XIV illustrates this transformation.

Scheme XIV

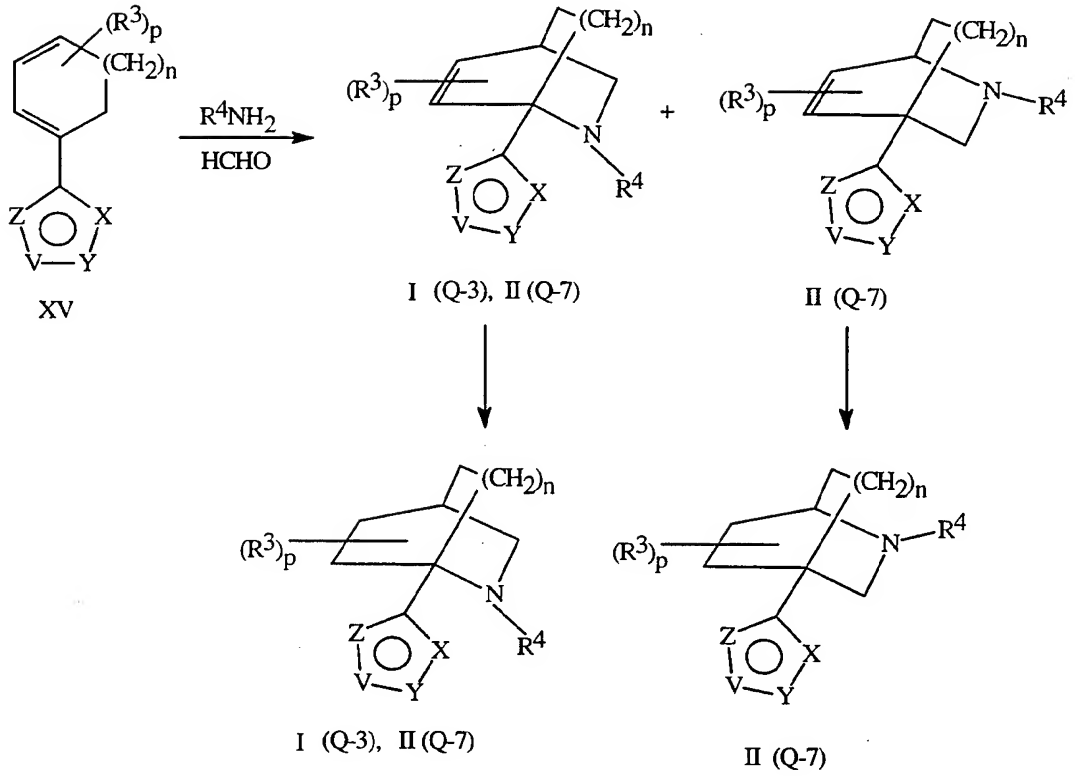


VII (where R^Z = H, alkyl)

XIII

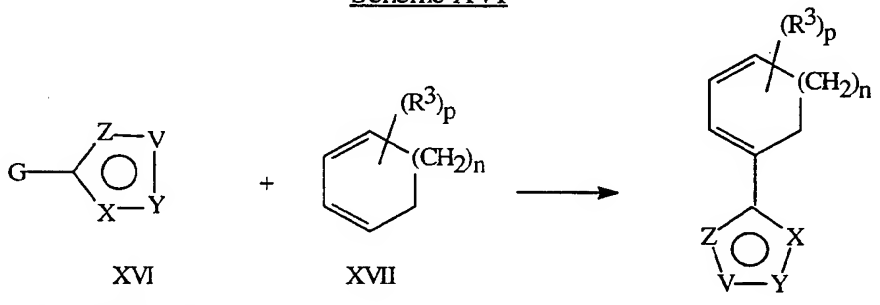
Formula I (Q-3) and Formula II (Q-7) compounds can be prepared by cycloaddition of compound XV using procedures known to one skilled in the art (*J. Am. Chem. Soc*, (1985) *107*, 1768). It will be recognized by one skilled in the art that fully saturated azabicyclic analogs can be prepared by simple reduction of the olefin by known methods. Scheme XV illustrates this transformation.

Scheme XV



Formula XV compounds can be prepared by reacting heterocycles of Formula XVI with olefins XVII under palladium catalysis in the presence of base. Typical solvents include acetonitrile, dimethylformamide, and tetrahydrofuran. Typical bases include triethylamine, diisopropylethylamine and sodium bicarbonate. Reaction temperatures range from room temperature to the reflux temperature of the particular solvent. Scheme XVI illustrates this transformation.

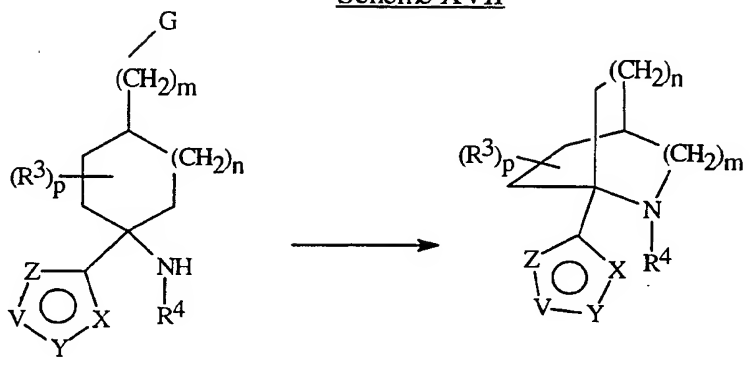
Scheme XVI



Alternatively, compounds of Formula I (Q-3) and Formula II (Q-7) can be prepared by intramolecular alkylation of Formula XVIII compounds by procedures

described for Formula I (Q-1) compounds. Scheme XVII illustrates this transformation.

Scheme XVII



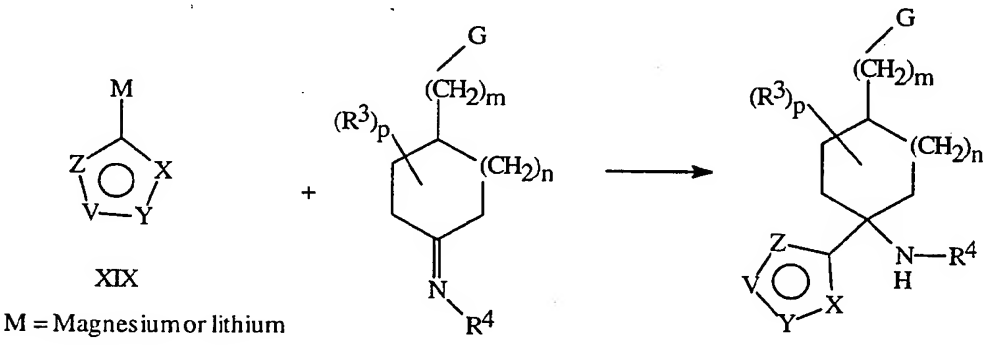
XVIII

G is halogen or sulfonate

I (Q-3) and II (Q-7)

Formula XVIII compounds can be prepared by addition of organometallic compounds of Formula XIX to imines XX. Typical solvents can include tetrahydrofuran and diethylether. Typical reaction temperatures range from -78°C to room temperature. Scheme XVIII illustrates this transformation.

Scheme XVIII



XIX

M = Magnesium or lithium

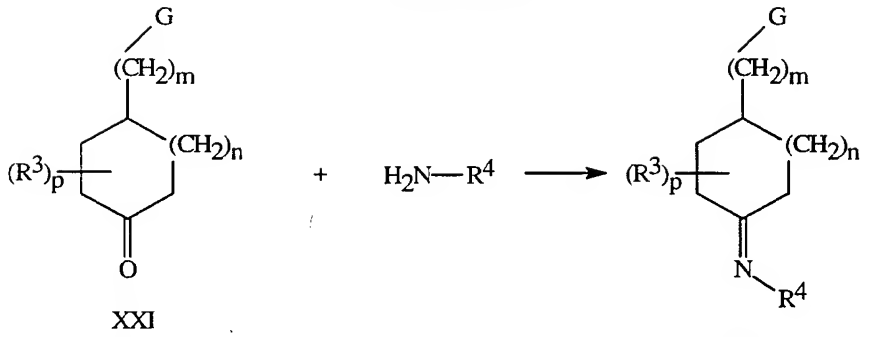
XX

G = halogen, hydroxyl, protected hydroxyl

XVIII

Imines of Formula XX can be prepared by condensation of a primary amine R^4NH_2 with ketones XXI under conditions known to one skilled in the art (March, J. *Advanced Organic Chemistry*; John Wiley & Sons, New York, 3rd ed. (1985) 465). Scheme XIX illustrates this transformation.

Scheme XIX



XXI

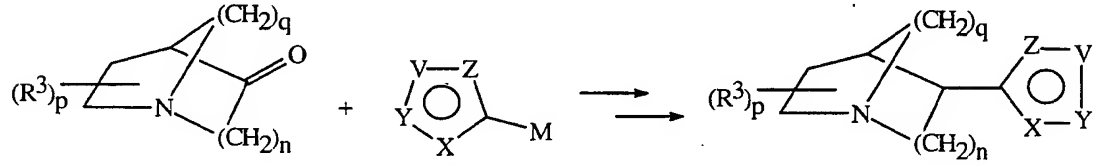
G= halogen, hydroxyl or protected hydroxyl

XX

Organometallic compounds of Formula XIX can be prepared by methods known in the art see, for example, EP 492,902-A1.

Compounds of Formula II (Q-6) can be synthesized by addition of organometallic compounds XIX to azabicyclic ketones XXII followed by chlorination, elimination, and hydrogenation as described in the art. See, for example, EP 412,798. Scheme XX depicts this transformation.

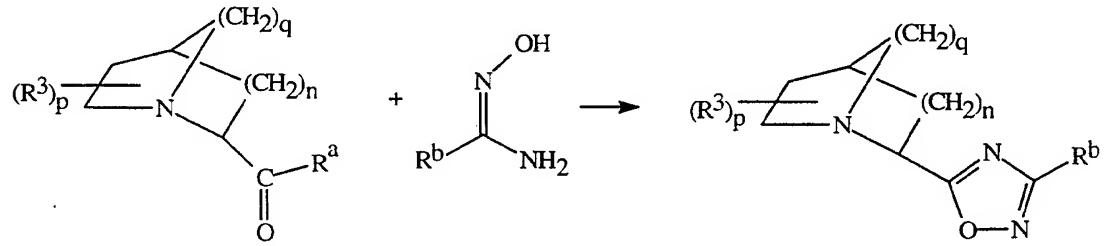
Scheme XX



XXII XIX II (Q-6)

Compounds of Formula II (Q-6) can be synthesized from azabicyclic esters XXIII and compounds XXIV, in a manner analogous to procedures described in the art. See, for example, EP 323,864. Scheme XXI depicts this transformation.

Scheme XXI



XXIII

R^a = OH, OMe, Cl

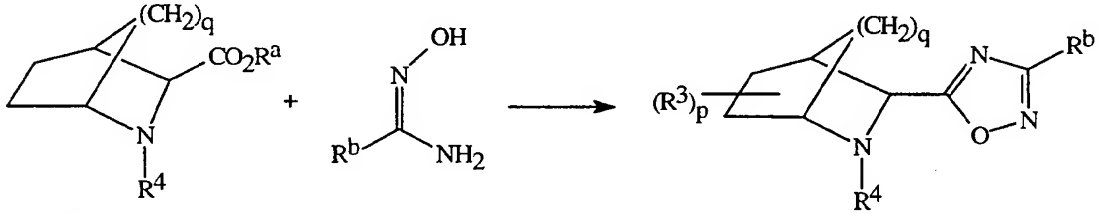
XXIV

R^b = alkyl, aryl, amino

II (Q-6)

Compounds of Formula II (Q-7) can be prepared from compounds of Formula XXV by procedures described for Formula II (Q-6) compounds. Scheme XXII depicts this transformation.

Scheme XXII

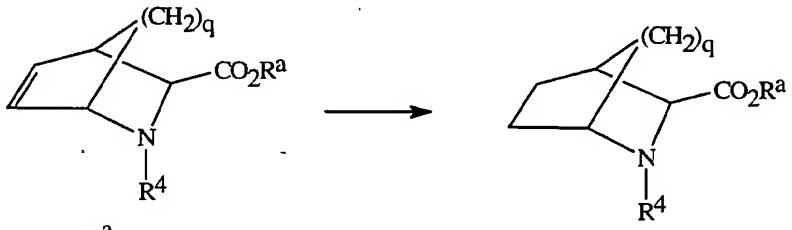


$R^a = C_1$-C_6 alkyl

XXV XXIV II (Q-7)

Compounds of Formula XXV can be prepared by hydrogenation of Formula XXVI compounds, which are described in the art (*J. Chem. Soc., Perkin Trans. 1* (1991), 1337). Scheme XXIII depicts this transformation.

Scheme XXIII

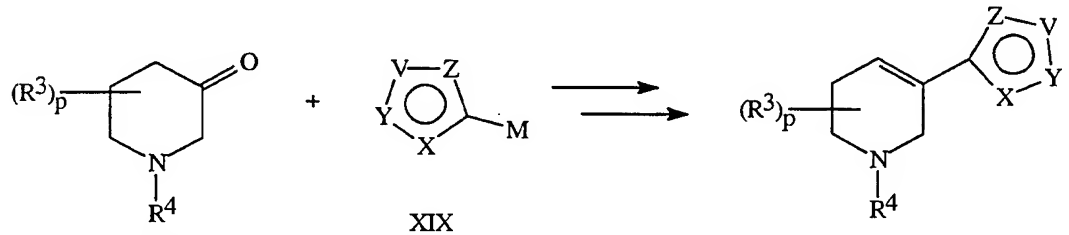


$R^a = C_1$-C_6 alkyl

XXVI XXV

Compounds of Formula II (Q-5) can be synthesized by addition of organometallic compounds XIX to azacyclic ketones XXVI, followed by chlorination and elimination. See, for example, *J. Med. Chem.* (1992) *35*, 4011. Scheme XXIV depicts this transformation.

Scheme XXIV

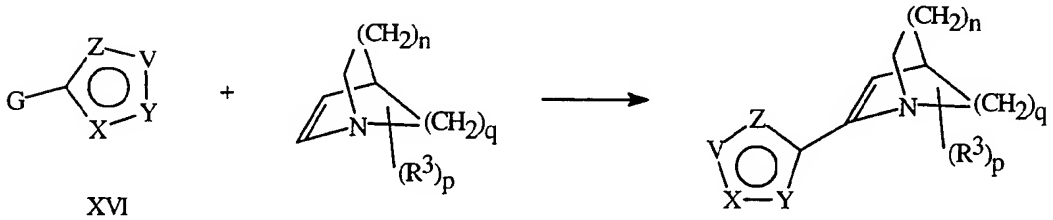


XXVI XIX II (Q-5)

M = Mg, Li

Compounds of Formula I (Q-4) and Formula II (Q-6) can be synthesized by reacting a heterocycle of Formula XVI with an olefin XXVII under palladium catalysis in the presence of base. Typical solvents include acetonitrile, dimethylformamide, tetrahydrofuran, and dimethylsulfoxide. Reaction temperatures range from room temperature to the reflux temperature of the particular solvent. Scheme XXV illustrates this transformation.

Scheme XXV



XVI
G= Br, I, OTf

XXVII

I (Q-4) and II (Q-6)

Olefins of the Formula XXVII can be prepared by using procedures known in the art (*Helv. Chim. Acta.* (1957) *40*, 2170).

It is recognized that some reagents and reaction conditions described above for preparing compounds of Formulae I and II may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences into the synthesis will aid in obtaining the desired products. The use and choice of appropriate protecting groups will be apparent to one skilled in chemical synthesis.

EXAMPLE 1

Preparation of 7-(6-chloro-3-pyridinyl)-1-azabicyclo[2.2.1]heptane

Step A: 6-Chloro-*N*-methoxy-*N*-methyl-3-pyridine carboxamide

To a suspension of 6-chloronicotinyl chloride (24.0 g, 0.136 mol) and *N,O*-dimethylhydroxylamine hydrochloride (14.0 g, 0.144 mol) in 200 mL of dichloromethane was added triethylamine (36.3 g, 0.358 mol) at 0°C. After complete addition, the reaction was warmed to room temperature and stirred for 2 h. Water was added and the mixture was extracted with dichloromethane . The organic layers were dried over $MgSO_4$, filtered and concentrated. Ether was added and the triethylamine hydrochloride salts were removed by filtration. Concentration of the ether solution gave 27.0 g of a yellow oil, sufficiently pure for the next step. ^1H NMR ($CDCl_3$) δ 8.78 (s,1H), 8.04 (d,1H), 7.40 (d,1H), 3.56 (s,3H), 3.40 (s,3H).

Step B: (6-Chloro-3-pyridinyl)(1-methyl-4-piperidinyl) methanone

Chloro(1-methyl-4-piperidinyl) magnesium (prepared from 4-chloro-1-methyl piperidine (17.75 g, 0.133 mol) in 300 mL of tetrahydrofuran and magnesium (3.4 g, 0.140 mol) according to the procedure in *J. Med. Chem.* (1965) *8*, 829), was added to a solution of the product of Step A (13.3 g, 0.066 mol) in 50 mL of tetrahydrofuran at 0°C. After addition was complete, the reaction was warmed to room temperature. After 1 h, dilute HCl solution was added and the mixture was extracted with ethyl acetate. The combined extracts were dried over $MgSO_4$, filtered and concentrated. The crude material was triturated with hexane to give 9.8 g of an off-white solid, m.p. 104.5-106°C. ^1H NMR ($CDCl_3$) δ 8.90 (s,1H), 8.20 (d,1H), 7.45 (d,1H), 3.20-3.05 (m,1H), 2.95 (d,2H), 2.31 (s,3H), 2.20-2.00 (m,2H), 2.00-1.80 (m,4H).

Step C: (6-Chloro-3-pyridinyl)(4-piperidinyl) methanone hydrochloride

To a solution of the product of Step B (6.28 g, 0.026 mol) in 100 mL of 1,2-dichloroethane was added 1-chloroethyl chloroformate (9.0 g, 0.063 mol). The mixture was heated at reflux for 3-4 h. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane. The combined extracts were dried over $MgSO_4$, filtered, and concentrated to give 8.0 g of a yellow solid. The crude solid was dissolved in methanol and heated at reflux for 30 min. After cooling to room temperature, the solvent was removed and the solids were triturated with ether to give 5.5 g (6-chloro-3-pyridinyl) (4-piperidinyl) methanone hydrochloride.

Step D: 2-Chloro-5-[chloro(4-piperidinyl)methyl] pyridine

Sodium borohydride (0.81 g, 0.021 mol) was added portionwise to a suspension of the product of Step C (5.5 g, 0.021 mol), in 50 mL of methanol. After complete addition, the reaction was stirred for 10 min and concentrated. The residue was suspended in 60 mL of dichloromethane/pyridine (5:1). Excess thionyl chloride (ca. 4 mL) was added. After 1 h, the mixture was concentrated. Water was added and the mixture was neutralized with potassium carbonate and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give 2.6 g of an off-white solid.

Step E: 7-(6-Chloro-3-pyridinyl)-1-azabicyclo[2.2.1] heptane

Potassium *t*-butoxide (2.5 g, 0.022 mol) was added to a suspension of the product of Step D (2.6 g, 0.009 mol) in 50 mL of tetrahydrofuran. The mixture was heated at reflux for 48 h. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The combined extracts were dried over $MgSO_4$, filtered, and concentrated. Chromatography on silica gel (9:1 chloroform:methanol) afforded 1.3 g of a yellow solid, m.p. 77-78°C. ^1H NMR ($CDCl_3$) δ 8.42 (s,1H), 7.75 (d,1H), 7.27 (s,1H), 3.75 (s,1H), 3.05 (dt,1H); 2.90 (d,1H), 2.70-2.60 (m,2H), 2.50-2.40 (m,1H), 1.9-1.7 (m,1H), 1.45-1.30 (m,2H), 1.20-1.10 (m,1H).

EXAMPLE 2

Preparation of 7-(3-pyridinyl)-1-azabicyclo[2.2.1]heptane

To a solution of 7-(6-chloro-3-pyridinyl)-1-azabicyclo [2.2.1]heptane (100.0 mg, 0.48 mmol) in methanol was added a catalytic amount of 5% palladium on carbon and a balloon containing hydrogen gas. After stirring overnight, the mixture was filtered through a pad of Celite® and concentrated. The residue was taken up in dichloromethane, washed with saturated sodium bicarbonate solution, dried over $MgSO_4$, filtered, and concentrated to give 55 mg of a brown oil. ^1H NMR ($CDCl_3$) δ 8.65 (s,1H), 8.50 (d,1H), 7.80 (d,1H), 7.25 (d,1H), 3.81 (s,1H), 3.10-3.00 (m,1H), 3.00-2.95 (m,1H), 2.80-2.60 (m,2H), 2.50-2.40 (m,1H), 1.90-1.80 (m,1H), 1.45-1.10 (m,3H).

EXAMPLE 3

Preparation of 7-(5,6-dichloro-3-pyridinyl)-1-azabicyclo[2.2.1]heptane

Step A: 5,6-Dichloro-*N*-methoxy-*N*-methyl-3-pyridine carboxamide

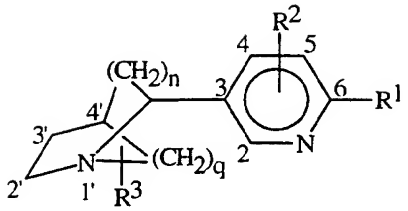
To a solution of 5,6-dichloronicotinic acid (10.0 g, 0.052 mmol) and triethylamine (15.2 mL, 0.109 mmol) in dichloromethane was added oxalyl chloride (6.94 g, 0.05 mmol). After the gas evolution ceased, *N,O*-dimethylhydroxylamine hydrochloride (5.34 g, 0.055 mmol) was added and the mixture was stirred overnight. Saturated sodium bicarbonate solution was added and the mixture was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated to give 9.1 g of a brown solid. ^1H NMR ($CDCl_3$) δ 8.68 (s,1H), 8.16 (s,1H), 3.59 (s,3H), 3.40 (s,3H)

Step B: 7-(5,6-Dichloro-3-pyridinyl)-1-azabicyclo[2.2.1]heptane

The product of Step A was manipulated according to Steps B-E of Example 1 to give 0.95 g of a waxy solid, m.p. 30-32°C. ^1H NMR ($CDCl_3$) δ 8.31 (s,1H), 7.88 (s,1H), 3.73 (s,1H), 3.05 (t,1H), 2.95-2.90 (m,1H), 2.7-2.6 (m,2H), 2.5-2.4 (m,1H), 1.9-1.8 (m,1H), 1.45-1.30 (m,2H), 1.3-1.2 (m,1H).

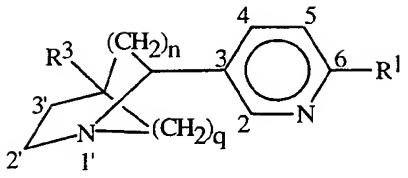
By the procedures described herein, the following compounds of Tables 1 to 23 can be prepared. The compounds in Table 1, line 1 can be referred to as 1-1, 1-2, 1-3, 1-4 and 1-5 (as designated by line and column). All the other specific compounds covered in these Tables can be designated in an analogous fashion. The following abbreviations have been used in Tables 1-23: Me = methyl, Et = ethyl, *i*Pr = isopropyl, nPr = n-propyl and Bn = benzyl.

Table 1



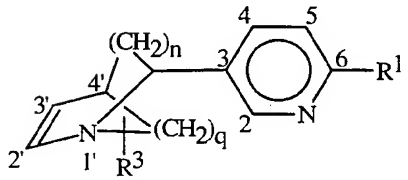
			COLUMN				
			1	2	3	4	5
1	n=0; q=2; R^2=H; R^3=H;	R^1=	F	Cl	Br	CH_3	H
2	n=1; q=2; R^2=H; R^3=H;	R^1=	F	Cl	Br	CH_3	H
3	n=0; q=2; R^2=5-Cl; R^3=H;	R^1=	F	Cl	Br	CH_3	H
4	n=1; q=2; R^2=5-Cl; R^3=H;	R^1=	F	Cl	Br	CH_3	H
5	n=0; q=2; R^2=5-F; R^3=H;	R^1=	F	Cl	Br	CH_3	H
6	n=1; q=2; R^2=5-F; R^3=H;	R^1=	F	Cl	Br	CH_3	H
7	n=0; q=2; R^2=5-CN; R^3=H;	R^1=	F	Cl	Br	CH_3	H
8	n=1; q=2; R^2=5-CN; R^3=H;	R^1=	F	Cl	Br	CH_3	H
9	n=1; q=1; R^2=H; R^3=H;	R^1=	F	Cl	Br	CH_3	H
10	n=1; q=1; R^2=5-Cl; R^3=H;	R^1=	F	Cl	Br	CH_3	H
11	n=1; q=1; R^2=5-F; R^3=H;	R^1=	F	Cl	Br	CH_3	H
12	n=1; q=1; R^2=5-CN; R^3=H;	R^1=	F	Cl	Br	CH_3	H
13	n=0; q=2; R^2=H; R^3=2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
14	n=1; q=2; R^2=H; R^3=2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
15	n=1; q=1; R^2=H; R^3=2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
16	n=0; q=2; R^2=H; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
17	n=1; q=2; R^2=H; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
18	n=1; q=1; R^2=H; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
19	n=0; q=2; R^2=H; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H
20	n=1; q=2; R^2=H; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H
21	n=1; q=1; R^2=H; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H

Table 2



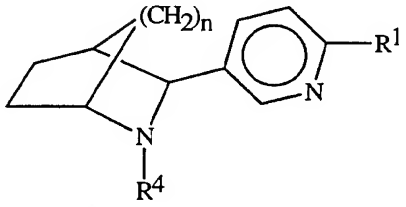
			COLUMN				
			1	2	3	4	5
22	n=0; q=2; R^3=Cl;	R^1=	F	Cl	Br	CH_3	H
23	n=1; q=2; R^3=Cl;	R^1=	F	Cl	Br	CH_3	H
24	n=1; q=1; R^3=Cl;	R^1=	F	Cl	Br	CH_3	H
25	n=0; q=2; R^3=Br;	R^1=	F	Cl	Br	CH_3	H
26	n=1; q=2; R^3=Br;	R^1=	F	Cl	Br	CH_3	H
27	n=1; q=1; R^3=Br;	R^1=	F	Cl	Br	CH_3	H
28	n=0; q=2; R^3=OH;	R^1=	F	Cl	Br	CH_3	H
29	n=1; q=2; R^3=OH;	R^1=	F	Cl	Br	CH_3	H
30	n=1; q=1; R^3=OH;	R^1=	F	Cl	Br	CH_3	H
31	n=0; q=2; R^3=NH_2;	R^1=	F	Cl	Br	CH_3	H
32	n=1; q=2; R^3=NH_2;	R^1=	F	Cl	Br	CH_3	H
33	n=1; q=1; R^3=NH_2;	R^1=	F	Cl	Br	CH_3	H
34	n=0; q=2; R^3=CN;	R^1=	F	Cl	Br	CH_3	H
35	n=1; q=2; R^3=CN;	R^1=	F	Cl	Br	CH_3	H
36	n=1; q=1; R^3=CN;	R^1=	F	Cl	Br	CH_3	H
37	n=0; q=2; R^3=CH_3;	R^1=	F	Cl	Br	CH_3	H
38	n=1; q=2; R^3=CH_3;	R^1=	F	Cl	Br	CH_3	H
39	n=1; q=1; R^3=CH_3;	R^1=	F	Cl	Br	CH_3	H
40	n=0; q=2; R^3=CO_2Me;	R^1=	F	Cl	Br	CH_3	H
41	n=1; q=2; R^3=CO_2Me;	R^1=	F	Cl	Br	CH_3	H
42	n=1; q=1; R^3=CO_2Me;	R^1=	F	Cl	Br	CH_3	H
43	n=0; q=2; R^3=CO_2H;	R^1=	F	Cl	Br	CH_3	H
44	n=1; q=2; R^3=CO_2H;	R^1=	F	Cl	Br	CH_3	H
45	n=1; q=1; R^3=CO_2H;	R^1=	F	Cl	Br	CH_3	H

Table 3



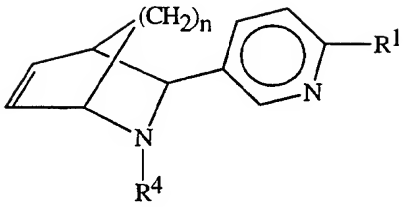
			COLUMN				
			1	2	3	4	5
46	n=0; q=2; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
47	n=1; q=2; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
48	n=1; q=1; R^3=3'-NO_2;	R^1=	F	Cl	Br	CH_3	H
49	n=0; q=2; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H
50	n=1; q=2; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H
51	n=1; q=1; R^3=3'-CN;	R^1=	F	Cl	Br	CH_3	H
52	n=0; q=2; R^3=3'-NO_2, 2'-NH_2;	R^1=	F	Cl	Br	CH_3	H
53	n=1; q=2; R^3=3'-NO_2, 2'-NH_2;	R^1=	F	Cl	Br	CH_3	H
54	n=1; q=1; R^3=3'-NO_2, 2'-NH_2;	R^1=	F	Cl	Br	CH_3	H
55	n=0; q=2; R^3=3'-NO_2, 2'NHMe;	R^1=	F	Cl	Br	CH_3	H
56	n=1; q=2; R^3=3'-NO_2, 2'-NHMe;	R^1=	F	Cl	Br	CH_3	H
57	n=1; q=1; R^3=3'-NO_2, 2'-NHMe;	R^1=	F	Cl	Br	CH_3	H
58	n=0; q=2; R^3=3'-NO_2, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
59	n=1; q=2; R^3=3'-NO_2, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
60	n=1; q=1; R^3=3'-NO_2, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
61	n=0; q=2; R^3=3'-CN, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
62	n=1; q=2; R^3=3'-CN, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H
63	n=1; q=1; R^3=3'-CN, 2'-CH_3;	R^1=	F	Cl	Br	CH_3	H

Table 4



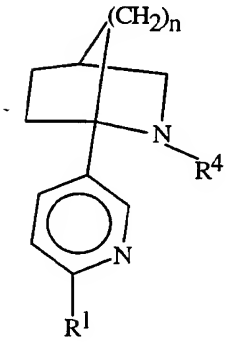
			COLUMN			
			1	2	3	4
64	R^4=H; n=1;	R^1=	Cl	Br	CH_3	H
65	R^4=H; n=2;	R^1=	Cl	Br	CH_3	H
66	R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3	H
67	R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3	H
68	R^4=Bn; n=1;	R^1=	Cl	Br	CH_3	H
69	R^4=Bn; n=2;	R^1=	Cl	Br	CH_3	H

Table 5



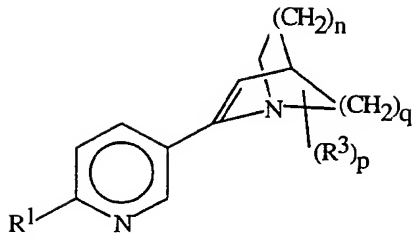
			COLUMN			
			1	2	3	4
70	R^4=H; n=1;	R^1=	Cl	Br	CH_3	H
71	R^4=H; n=2;	R^1=	Cl	Br	CH_3	H
72	R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3	H
73	R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3	H
74	R^4=Bn; n=1;	R^1=	Cl	Br	CH_3	H
75	R^4=Bn; n=2;	R^1=	Cl	Br	CH_3	H

Table 6



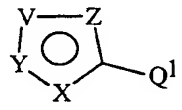
			COLUMN			
			1	2	3	4
76	R^4=H; n=1;	R^1=	Cl	Br	CH_3	H
77	R^4=H; n=2;	R^1=	Cl	Br	CH_3	H
78	R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3	H
79	R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3	H
80	R^4=Bn; n=1;	R^1=	Cl	Br	CH_3	H
81	R^4=Bn; n=2;	R^1=	Cl	Br	CH_3	H

Table 7

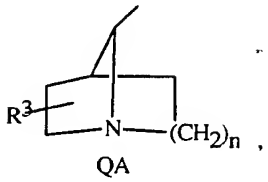


			COLUMN				
			1	2	3	4	5
82	n=1; q=1	R^1=	F	Cl	Br	CH_3	H
83	n=1, q=2	R^1=	F	Cl	Br	CH_3	H
84	n=0, q=3	R^1=	F	Cl	Br	CH_3	H

Key for Tables 8-23



where Q^1=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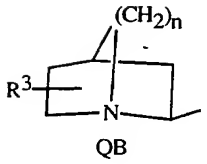
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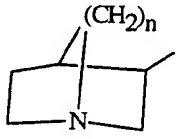
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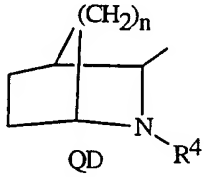
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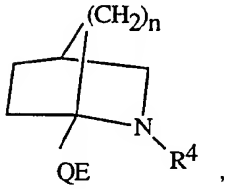
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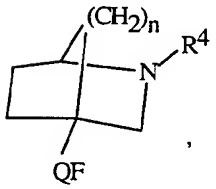
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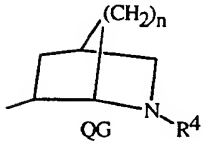
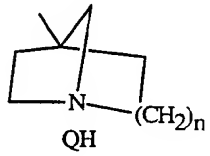

QG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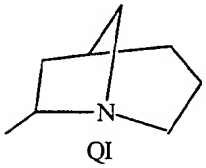
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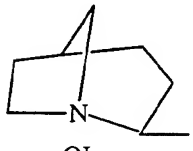
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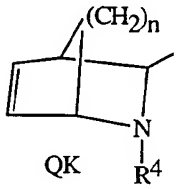
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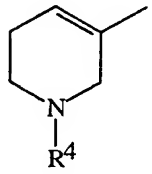
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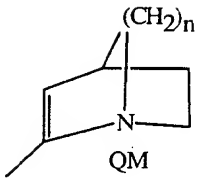
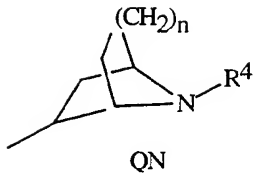


QM



QN

Table 8

	Q^1=QA		COLUMN 1	2	3	4	5
85	Z=O; V=N; Y=CR^1; X=N; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
86	Z=O; V=N; Y=CR^1; X=N; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
87	Z=O; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
88	Z=O; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
89	Z=O; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
90	Z=O; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
91	Z=O; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
92	Z=O; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
93	Z=O; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
94	Z=O; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
95	Z=S; V=N; Y=CR^1; X=N; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
96	Z=S; V=N; Y=CR^1; X=N; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
97	Z=S; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
98	Z=S; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
99	Z=S; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
100	Z=S; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
101	Z=S; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
102	Z=S; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
103	Z=S; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
104	Z=S; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
105	Z=N; V=N; Y=CR^1; X=O; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
106	Z=N; V=N; Y=CR^1; X=O; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
107	Z=N; V=N; Y=CR^1; X=O; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
108	Z=N; V=N; Y=CR^1; X=O; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
109	Z=N; V=N; Y=CR^1; X=O; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
110	Z=N; V=N; Y=CR^1; X=O; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
111	Z=N; V=N; Y=CR^1; X=O; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
112	Z=N; V=N; Y=CR^1; X=O; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
113	Z=N; V=N; Y=CR^1; X=O; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2

114	Z=N; V=N; Y=CR^1; X=O; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
115	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
116	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
117	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
118	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
119	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
120	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
121	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
122	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
123	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
124	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
125	Z=CH; V=N; Y=CR^1; X=S; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
126	Z=CH; V=N; Y=CR^1; X=S; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
127	Z=CH; V=N; Y=CR^1; X=S; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
128	Z=CH; V=N; Y=CR^1; X=S; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
129	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
130	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
131	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
132	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
133	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
134	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
135	Z=O; V=N; Y=CR^1; X=CH; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
136	Z=O; V=N; Y=CR^1; X=CH; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
137	Z=O; V=N; Y=CR^1; X=CH; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
138	Z=O; V=N; Y=CR^1; X=CH; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
139	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
140	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
141	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
142	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
143	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
144	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
145	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
146	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
147	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
148	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
149	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
150	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
151	Z=N; V=CR^2; Y=C(R^1)=N; X=CH; R^2=H; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H

152	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
153	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
154	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
155	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=F; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
156	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=F; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
157	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=Cl; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
158	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=Cl; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
159	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=H; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
160	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=H; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
161	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=2'-CH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
162	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=2'-CH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
163	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-OCH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
164	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-OCH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
165	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-Cl; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
166	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-Cl; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
167	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-CH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
168	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-CH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H

Table 9

	Q^1=QB		COLUMN				
			1	2	3	4	5
169	Z=O; V=N; Y=CR^1; X=N; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
170	Z=O; V=N; Y=CR^1; X=N; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
171	Z=O; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
172	Z=O; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
173	Z=O; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
174	Z=O; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
175	Z=O; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
176	Z=O; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
177	Z=O; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
178	Z=O; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
179	Z=S; V=N; Y=CR^1; X=N; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
180	Z=S; V=N; Y=CR^1; X=N; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
181	Z=S; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
182	Z=S; V=N; Y=CR^1; X=N; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
183	Z=S; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
184	Z=S; V=N; Y=CR^1; X=N; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2

185	Z=S; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
186	Z=S; V=N; Y=CR^1; X=N; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
187	Z=S; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
188	Z=S; V=N; Y=CR^1; X=N; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
189	Z=N; V=N; Y=CR^1; X=O; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
190	Z=N; V=N; Y=CR^1; X=O; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
191	Z=N; V=N; Y=CR^1; X=O; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
192	Z=N; V=N; Y=CR^1; X=O; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
193	Z=N; V=N; Y=CR^1; X=O; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
194	Z=N; V=N; Y=CR^1; X=O; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
195	Z=N; V=N; Y=CR^1; X=O; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
196	Z=N; V=N; Y=CR^1; X=O; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
197	Z=N; V=N; Y=CR^1; X=O; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
198	Z=N; V=N; Y=CR^1; X=O; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
199	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
200	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
201	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
202	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
203	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
204	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
205	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
206	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
207	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
208	Z=CH; V=N; Y=$C(R^1)$=N; X=CH; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
209	Z=CH; V=N; Y=CR^1; X=S; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
210	Z=CH; V=N; Y=CR^1; X=S; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
211	Z=CH; V=N; Y=CR^1; X=S; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
212	Z=CH; V=N; Y=CR^1; X=S; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
213	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
214	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
215	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
216	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
217	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
218	Z=CH; V=N; Y=CR^1; X=S; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
219	Z=O; V=N; Y=CR^1; X=CH; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
220	Z=O; V=N; Y=CR^1; X=CH; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
221	Z=O; V=N; Y=CR^1; X=CH; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
222	Z=O; V=N; Y=CR^1; X=CH; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H

223	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
224	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
225	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
226	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
227	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
228	Z=O; V=N; Y=CR^1; X=CH; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
229	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
230	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
231	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=2'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
232	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=2'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
233	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-OCH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
234	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-OCH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
235	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-Cl; n=1;	R^1=	F	Cl	Br	CH_3	H
236	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-Cl; n=2;	R^1=	F	Cl	Br	CH_3	H
237	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-CH_3; n=1;	R^1=	F	Cl	Br	CH_3	H
238	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=H; R^3=4'-CH_3; n=2;	R^1=	F	Cl	Br	CH_3	H
239	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=F; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
240	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=F; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
241	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=Cl; R^3=H; n=1;	R^1=	F	Cl	Br	CH_3	H
242	Z=N; V=CR^2; Y=$C(R^1)$=N; X=CH; R^2=Cl; R^3=H; n=2;	R^1=	F	Cl	Br	CH_3	H
243	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=H; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
244	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=H; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
245	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=2'-CH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
246	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=2'-CH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
247	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-OCH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
248	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-OCH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
249	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-Cl; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
250	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-Cl; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H
251	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-CH_3; n=1;	R^{11}=	CH_3	Et	iPr	nPr	H
252	Z=CH; V=N; Y=NR^{11}; X=CH; R^3=4'-CH_3; n=2;	R^{11}=	CH_3	Et	iPr	nPr	H

Table 10

	Q^1=QC		COLUMN				
			1	2	3	4	5
253	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
254	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
255	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
256	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H

257	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
258	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
259	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
260	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
261	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
262	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
263	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
264	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
265	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
266	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
267	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
268	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
269	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
270	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
271	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
272	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
273	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
274	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
275	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
276	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
277	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
278	Z=CH; V=CH; Y=NR^{11}; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
279	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
280	Z=CH; V=N; Y=NR^{11}; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 11

			COLUMN				
	Q^1=QD		1	2	3	4	5
281	Z=O; V=N; Y=CR^1; X=N; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
282	Z=O; V=N; Y=CR^1; X=N; R^4=CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
283	Z=O; V=N; Y=CR^1; X=N; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
284	Z=O; V=N; Y=CR^1; X=N; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
285	Z=O; V=N; Y=CR^1; X=N; R^4=CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
286	Z=O; V=N; Y=CR^1; X=N; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
287	Z=S; V=N; Y=CR^1; X=N; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
288	Z=S; V=N; Y=CR^1; X=N; R^4=CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2

289	Z=S; V=N; Y=CR^1; X=N; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
290	Z=S; V=N; Y=CR^1; X=N; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
291	Z=S; V=N; Y=CR^1; X=N; R^4=CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
292	Z=S; V=N; Y=CR^1; X=N; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
293	Z=N ; V=N; Y=CR^1; X=O; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
294	Z=N ; V=N; Y=CR^1; X=O; R^4=CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
295	Z=N ; V=N; Y=CR^1; X=O; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
296	Z=N ; V=N; Y=CR^1; X=O; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
297	Z=N ; V=N; Y=CR^1; X=O; R^4=CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
298	Z=N ; V=N; Y=CR^1; X=O; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
299	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
300	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
301	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
302	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
303	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
304	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
305	Z=CH; V=N; Y=CR^1; X=S; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
306	Z=CH; V=N; Y=CR^1; X=S; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
307	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
308	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
309	Z=O; V=N; Y=CR^1; X=CH; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
310	Z=O; V=N; Y=CR^1; X=CH; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
311	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
312	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
313	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
314	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
315	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
316	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
317	Z=CH; V=N; Y=CR^1; X=S; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
318	Z=CH; V=N; Y=CR^1; X=S; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
319	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
320	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
321	Z=O; V=N; Y=CR^1; X=CH; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
322	Z=O; V=N; Y=CR^1; X=CH; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		
323	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
324	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
325	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=CH_3; n=1;	R^1=	Cl	Br	CH_3		
326	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=CH_3; n=2;	R^1=	Cl	Br	CH_3		

327	Z=CH; V=N; Y=NR[11]; X=CH; R[4]=H, n=1;	R[11]=	CH_3	iPr	Et	
328	Z=CH; V=N; Y=NR[11]; X=CH; R[4]=H, n=2;	R[11]=	CH_3	iPr	Et	
329	Z=CH; V=N; Y=NR[11]; X=CH; R[4]=CH_3, n=1;	R[11]=	CH_3	iPr	Et	
330	Z=CH; V=N; Y=NR[11]; X=CH; R[4]=CH_3, n=2;	R[11]=	CH_3	iPr	Et	

Table 12

Q^1=QE R^4=CH_3

			COLUMN		
			1	2	3
331	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	Cl	Br	CH_3
332	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	Cl	Br	CH_3
333	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	Cl	Br	CH_3
334	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	Cl	Br	CH_3
335	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	Cl	Br	CH_3
336	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	Cl	Br	CH_3
337	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	Cl	Br	CH_3
338	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	Cl	Br	CH_3
339	Z=O; V=N; Y=CR^1; X=N; n=1;	R^1=	Cl	NH_2	CH_3
340	Z=O; V=N; Y=CR^1; X=N; n=2;	R^1=	Cl	NH_2	CH_3
341	Z=S; V=N; Y=CR^1; X=N; n=1;	R^1=	Cl	NH_2	CH_3
342	Z=S; V=N; Y=CR^1; X=N; n=2;	R^1=	Cl	NH_2	CH_3
343	Z=CH; V=N; Y=NCH_3; X=CH; n=1;	R^1=	Cl	NH_2	CH_3
344	Z=CH; V=N; Y=NCH_3; X=CH; n=2;	R^1=	Cl	NH_2	CH_3

Table 13

Q^1=QF; R^4=CH_3

			COLUMN				
			1	2	3	4	5
345	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
346	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
347	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
348	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
349	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
350	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
351	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
352	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
353	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
354	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H

355	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
356	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
357	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
358	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
359	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
360	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
361	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
362	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
363	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
364	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
365	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
366	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
367	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
368	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
369	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
370	Z=CH; V=CH; Y=NR^{11}; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
371	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
372	Z=CH; V=N; Y=NR^{11}; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 14

	Q^1=QG; R^4=H		COLUMN				
			1	2	3	4	5
373	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
374	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
375	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
376	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
377	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
378	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
379	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
380	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
381	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
382	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
383	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
384	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
385	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
386	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
387	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H

388	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
389	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
390	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
391	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
392	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
393	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
394	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
395	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
396	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
397	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
398	Z=CH; V=CH; Y=NR^{11}; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
399	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
400	Z=CH; V=N; Y=NR^{11}; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 15

Q^1=QG; R^4=CH_3

			COLUMN				
			1	2	3	4	5
401	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
402	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
403	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
404	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
405	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
406	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
407	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
408	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
409	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
410	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
411	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
412	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
413	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
414	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
415	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
416	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
417	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
418	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
419	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
420	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H

421	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
422	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
423	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
424	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
425	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
426	Z=CH; V=CH; Y=NR^{11}; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
427	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
428	Z=CH; V=N; Y=NR^{11}; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 16

	Q^1=QH		COLUMN				
			1	2	3	4	5
429	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
430	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
431	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
432	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
433	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
434	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
435	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
436	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
437	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
438	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
439	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
440	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
441	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
442	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
443	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
444	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
445	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
446	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
447	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
448	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
449	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
450	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
451	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
452	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
453	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

454	Z=CH; V=CH; Y=NR[11]; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
455	Z=CH; V=N; Y=NR[11]; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
456	Z=CH; V=N; Y=NR[11]; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 17

	Q^1=QI		COLUMN		
			1	2	3
457	Z=CH; V=N; Y=C(R^1)=N; X=CH;	R^1=	Cl	Br	CH_3
458	Z=CH; V=N; Y=CR^1; X=S;	R^1=	Cl	Br	CH_3
459	Z=O; V=N; Y=CR^1; X=CH;	R^1=	Cl	Br	CH_3
460	Z=N; V=CH; Y=C(R^1)=N; X=CH;	R^1=	Cl	Br	CH_3
461	Z=O; V=N; Y=CR^1; X=N;	R^1=	Cl	Br	CH_3
462	Z=S; V=N; Y=CR^1; X=N;	R^1=	Cl	Br	CH_3
463	Z=CH; V=N; Y=NCH_3; X=CH;	R^1=	Cl	Br	CH_3

Table 18

	Q^1=QJ		COLUMN		
			1	2	3
464	Z=CH; V=N; Y=C(R^1)=N; X=CH;	R^1=	Cl	Br	CH_3
465	Z=CH; V=N; Y=CR^1; X=S;	R^1=	Cl	Br	CH_3
466	Z=O; V=N; Y=CR^1; X=CH;	R^1=	Cl	Br	CH_3
467	Z=N; V=CH; Y=C(R^1)=N; X=CH;	R^1=	Cl	Br	CH_3
468	Z=O; V=N; Y=CR^1; X=N;	R^1=	Cl	Br	CH_3
469	Z=S; V=N; Y=CR^1; X=N;	R^1=	Cl	Br	CH_3
470	Z=CH; V=N; Y=NCH_3; X=CH;	R^1=	Cl	Br	CH_3

Table 19

	Q^1=QK		COLUMN				
			1	2	3	4	5
471	Z=O; V=N; Y=CR^1; X=N; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
472	Z=O; V=N; Y=CR^1; X=N; R^4=CH_3; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
473	Z=O; V=N; Y=CR^1; X=N; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
474	Z=O; V=N; Y=CR^1; X=N; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
475	Z=O; V=N; Y=CR^1; X=N; R^4=CH_3; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
476	Z=O; V=N; Y=CR^1; X=N; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
477	Z=S; V=N; Y=CR^1; X=N; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2

478	Z=S; V=N; Y=CR^1; X=N; R^4=CH$_3$; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
479	Z=S; V=N; Y=CR^1; X=N; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
480	Z=S; V=N; Y=CR^1; X=N; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
481	Z=S; V=N; Y=CR^1; X=N; R^4=CH$_3$; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
482	Z=S; V=N; Y=CR^1; X=N; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
483	Z=N ; V=N; Y=CR^1; X=O; R^4=H; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
484	Z=N ; V=N; Y=CR^1; X=O; R^4=CH$_3$; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
485	Z=N ; V=N; Y=CR^1; X=O; R^4=Bn; n=1;	R^1=	F	Cl	Br	CH_3	NH_2
486	Z=N ; V=N; Y=CR^1; X=O; R^4=H; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
487	Z=N ; V=N; Y=CR^1; X=O; R^4=CH$_3$; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
488	Z=N ; V=N; Y=CR^1; X=O; R^4=Bn; n=2;	R^1=	F	Cl	Br	CH_3	NH_2
489	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
490	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
491	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH$_3$; n=1;	R^1=	Cl	Br	CH_3		
492	Z=CH; V=N; Y=C(R^1)=N; X=CH; R^4=CH$_3$; n=2;	R^1=	Cl	Br	CH_3		
493	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
494	Z=CH; V=N; Y=CR^1; X=S; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
495	Z=CH; V=N; Y=CR^1; X=S; R^4=CH$_3$; n=1;	R^1=	Cl	Br	CH_3		
496	Z=CH; V=N; Y=CR^1; X=S; R^4=CH$_3$; n=2;	R^1=	Cl	Br	CH_3		
497	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
498	Z=O; V=N; Y=CR^1; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
499	Z=O; V=N; Y=CR^1; X=CH; R^4=CH$_3$; n=1;	R^1=	Cl	Br	CH_3		
500	Z=O; V=N; Y=CR^1; X=CH; R^4=CH$_3$; n=2;	R^1=	Cl	Br	CH_3		
501	Z=CH; V=N; Y=NR^{11}; X=CH; R^4=H, n=1;	R^{11}=	CH_3	Et	iPr		
502	Z=CH; V=N; Y=NR^{11}; X=CH; R^4=H, n=2;	R^{11}=	CH_3	Et	iPr		
503	Z=CH; V=N; Y=NR^{11}; X=CH; R^4=CH$_3$, n=1;	R^{11}=	CH_3	Et	iPr		
504	Z=CH; V=N; Y=NR^{11}; X=CH; R^4=CH$_3$, n=2;	R^{11}=	CH_3	Et	iPr		
505	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=H; n=1;	R^1=	Cl	Br	CH_3		
506	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=H; n=2;	R^1=	Cl	Br	CH_3		
507	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=CH$_3$; n=1;	R^1=	Cl	Br	CH_3		
508	Z=N; V=CH; Y=C(R^1)=N; X=CH; R^4=CH$_3$; n=2;	R^1=	Cl	Br	CH_3		

Table 20

	Q^1=QL		COLUMN 1	2	3	4	5
509	Z=S; V=CH; Y=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
510	Z=S; V=CH; Y=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
511	Z=O; V=CH; Y=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
512	Z=O; V=CH; Y=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
513	Z=CR^1; V=CH; Y=O; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
514	Z=CR^1; V=CH; Y=O; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
515	Z=CR^1; V=S; Y=CH; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
516	Z=CR^1; V=S; Y=CH; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
517	Z=CR^1; V=O; Y=CH; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
518	Z=CR^1; V=O; Y=CH; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
519	Z=CH; V=S; Y=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
520	Z=CH; V=S; Y=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
521	Z=CH; V=O; Y=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
522	Z=CH; V=O; Y=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
523	Z=CR^1; V=CH=CH; Y=CH; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
524	Z=CR^1; V=CH=CH; Y=CH; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
525	Z=CR^1; V=CH=CH; Y=CH; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
526	Z=CR^1; V=N; Y=CH=CH; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
527	Z=CR^1; V=N; Y=CH=CH; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
528	Z=CH; V=CH=CH; Y=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
529	Z=CH; V=CH=CH; Y=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
530	Z=CH; V=N; Y=CH=CR^1; X=N, R^4=CH_3;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
531	Z=CH; V=N; Y=CH=CR^1; X=N, R^4=H;	R^1=	H	Cl	CH_3	OCH_3	O-n-hexyl
532	Z=CH; V=CH; Y=NR^{11}; X=N, R^4=CH_3;	R^{11}=	H	Me	Et	iPr	nPr
533	Z=CH; V=CH; Y=NR^{11}; X=N, R^4=H;	R^{11}=	H	Me	Et	iPr	nPr

Table 21

	Q^1=QM		COLUMN 1	2	3	4	5
534	Z=CH; V=N; Y=CR^1=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
535	Z=CH; V=N; Y=CR^1=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
536	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
537	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H

538	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
539	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
540	Z=N; V=CH; Y=CR^1=N; X=N; n=1;	R^1=	F	Cl	Br	CH_3	H
541	Z=N; V=CH; Y=CR^1=N; X=N; n=2;	R^1=	F	Cl	Br	CH_3	H
542	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	H	CH_3	C_2H_5	iPr	nPr
543	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	H	CH_3	C_2H_5	iPr	nPr

Table 22

Q^1=QN R^4=H

			COLUMN				
			1	2	3	4	5
544	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
545	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
546	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
547	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
548	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
549	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
550	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
551	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
552	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
553	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
554	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
555	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
556	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
557	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
558	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
559	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
560	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
561	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
562	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
563	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
564	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
565	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
566	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
567	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
568	Z=CH; V=CH; Y=NR^{11}; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
569	Z=CH; V=CH; Y=NR^{11}; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
570	Z=CH; V=N; Y=NR^{11}; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

571	Z=CH; V=N; Y=NR[11]; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Table 23

	Q^1=QN R^4=CH_3		COLUMN				
			1	2	3	4	5
572	Z=S; V=CH; Y=CR^1; X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
573	Z=S; V=CH; Y=CR^1; X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
574	Z=O; V=CH; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
575	Z=O; V=CH; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
576	Z=CH; V=S; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
577	Z=CH; V=S; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
578	Z=CH; V=O; Y=CR^1, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
579	Z=CH; V=O; Y=CR^1, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
580	Z=CR^1; V=CH; Y=O, X=N, n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
581	Z=CR^1; V=CH; Y=O, X=N, n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
582	Z=CH; V=CH=CH; Y=CR^1; X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
583	Z=CH; V=CH=CH; Y=CR^1; X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
584	Z=CH; V=N; Y=CH=C(R^1); X=N; n=1;	R^1=	CH_3	OCH_3	NH_2	Cl	H
585	Z=CH; V=N; Y=CH=C(R^1); X=N; n=2;	R^1=	CH_3	OCH_3	NH_2	Cl	H
586	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
587	Z=CH; V=N; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
588	Z=CH; V=N; Y=CR^1; X=S; n=1;	R^1=	F	Cl	Br	CH_3	H
589	Z=CH; V=N; Y=CR^1; X=S; n=2;	R^1=	F	Cl	Br	CH_3	H
590	Z=O; V=N; Y=CR^1; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
591	Z=O; V=N; Y=CR^1; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
592	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
593	Z=N; V=CH; Y=C(R^1)=N; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
594	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=1;	R^1=	F	Cl	Br	CH_3	H
595	Z=CH; V=N; Y=C(R^1)=CH; X=CH; n=2;	R^1=	F	Cl	Br	CH_3	H
596	Z=CH; V=CH; Y=NR[11]; X=N; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
597	Z=CH; V=CH; Y=NR[11]; X=N; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
598	Z=CH; V=N; Y=NR[11]; X=CH; n=1;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr
599	Z=CH; V=N; Y=NR[11]; X=CH; n=2;	R^{11}=	CH_3	C_2H_5	H	iPr	nPr

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent. Useful formulations

include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like, consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 weight percent.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Wettable Powders	5-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, and the like.

Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-148, *Perry's*

Chemical Engineer's Handbook, 4th ed., McGraw-Hill, New York, (1963), pp 8-57 and following, and WO 91/13546.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138 -140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, (1961), pp 81-96; and Hance et al., *Weed Control Handbook*, 8th ed., Blackwell Scientific Publications, Oxford, (1989).

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Table A.

Example A

Wettable Powder

Compound 1	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 1	10.0%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 1	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

Compound 1	20.0%
blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, stem or root feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropods" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all growth stages of all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, junveniles and adults of the Phylum Nematoda. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Siphonaptera, Blattaria, Thysanura and Psocoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. Specifically, the compounds are active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrosteles fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera frugiperda*), black bean aphid (*Aphis fabae*), green peach aphid (*Myzus persica*), cotton aphid (*Aphis gossypii*), Russian wheat aphid (*Diuraphis noxia*), English grain aphid (*Sitobion avenae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug (*Scotinophara lurida*), rice stink bug (*Oebalus pugnax*), rice bug (*Leptocorisa chinensis*), slender rice bug (*Cletus puntiger*), and southern green stink bug (*Nezara viridula*). The compounds are active on mites, demonstrating ovicidal, larvicidal and chemosterilant activity against such families as Tetranychidae including *Tetranychus urticae, Tetranychus cinnabarinus, Tetranychus mcdanieli, Tetranychus pacificus, Tetranychus turkestani, Byrobia rubrioculus, Panonychus ulmi, Panonychus citri, Eotetranychus carpini borealis, Eotetranychus, hicoriae, Eotetranychus sexmaculatus, Eotetranychus yumensis, Eotetranychus banksi* and *Oligonychus pratensis*; Tenuipalpidae including *Brevipalpus lewisi, Brevipalpus phoenicis, Brevipalpus californicus* and *Brevipalpus obovatus*; Eriophyidae including *Phyllocoptruta oleivora, Eriophyes sheldoni, Aculus cornutus, Epitrimerus pyri* and

Eriophyes mangiferae. See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as avermectin B, monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, metha-midophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, tefluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, imidacloprid, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl, captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconzole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracyline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate, dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as entomopathogenic bacteria, virus and fungi.

In certain instances, combinations with other arthropodicides having a similiar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Arthropod pests are controlled and protection of agronomic, horticultural and specialty crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Thus, the present invention further comprises a method for the control of foliar and soil inhabiting arthropods and

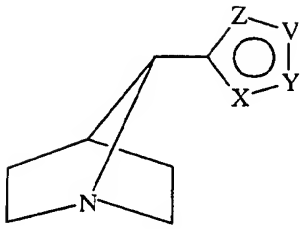
nematode pests and protection of agronomic and/or nonagronomic crops, comprising applying one or more of the compounds of Formula I or Formula II, or compositions containing at least one such compound, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, seed coats, microencapsulations, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, dusts and many others. The compounds can be incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, and synergists and other solvents such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

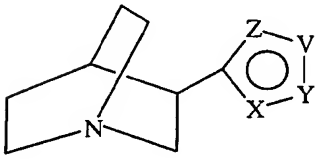
The following TESTS demonstrate the control efficacy of compounds of this invention on specific pests. "Control efficacy" represents inhibition of arthropod development (including mortality) that causes significantly reduced feeding. The pest control protection afforded by the compounds is not limited, however, to these species. See Index Tables A-D for compound descriptions.

Index Table A



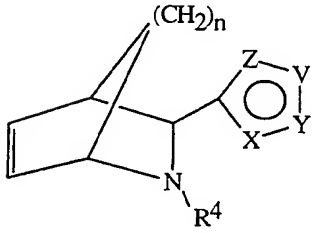
Compound	Z	V	Y	X	m.p. °C
1	CH	N	C(Cl)=CH	CH	77-78
2	CH	N	CH=CH	CH	oil[a]
3	CH	N	C(Cl)=C(Cl)	CH	30-32
4	N	CH	$C(CH_3)$=N	CH	oil[b]

Index Table B



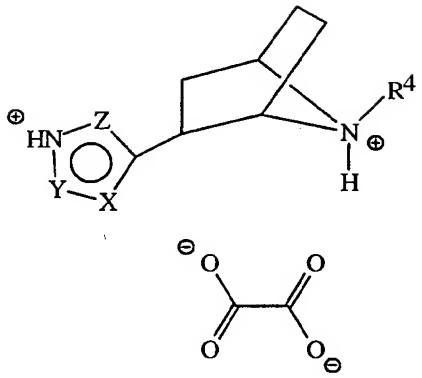
Compound	Z	V	Y	X	m.p. °C
5	N	CH	CH=N	CH	45-50

Index Table C



Compound	Z	V	Y	X	R^4	n	m.p. °C
6	O	N	$C(CH_3)$	N	Bn	1	oil[c]
7	CH	N	CH=CH	CH	CH_3	2	oil[d]

Index Table D



Compound	Z	Y	X	R^4	m.p. °C
8	CH	C(Cl)=CH	CH	H	159-161

^{1}H NMR ($CDCl_3$ DATA)

a δ 8.65 (s,1H), 8.50 (d,1H), 7.80 (d,1H), 7.25 (d,1H), 3.81 (s,1H), 3.10-3.00 (m,1H), 3.00-2.95 (m,1H), 2.80-2.60 (m,2H), 2.50-2.40 (m,1H), 1.90-1.80 (m,1H), 1.45-1.10 (m,3H).

b δ 8.68 (s,1H), 8.39 (s,1H), 3.87 (s,1H), 3.2-3.1 (m,2H), 2.85-2.65 (m,2H), 2.55 (s,3H), 2.6-2.5 (m,1H), 1.9-1.8 (m,1H), 1.5-1.2 (m,3H).

c δ 7.35-7.2 (m,5H), 6.6 (dd,1H), 6.4 (dd,1H), 3.97 (s,1H), 3.6 (ABq,2H), 3.2 (s,1H), 3.0 (s,1H), 2.34 (s,3H), 2.05 (d,1H), 1.55 (d,1H).

d δ 8.66 (s,1H), 8.45 (d,1H), 7.8 (d,1H), 7.8 (d,1H), 7.25-7.20 (m,1H), 6.6 (dd,1H), 6.4 (dd,1H), 3.45-3.40 (m,1H), 3.0 (s,1H), 2.45-2.40 (m,1H), 2.17 (s,3H), 2.05-1.95 (m,1H), 1.4-1.2 (m,2H), 0.95-0.80 (m,1H).

TEST A

Fall Armyworm

Test units, each consisting of a H.I.S. (high impact styrene) tray with 16 cells were prepared. Wet filter paper and approximately 8 cm^2 of lima bean leaf was placed into twelve of the cells. A 0.5 cm layer of wheat germ diet was placed into the four remaining cells. Fifteen to twenty third-instar larvae of fall armyworm (*Spodoptera frugiperda*) were placed into an 8 ounce (230 mL) plastic cup. Solutions of each of the test compounds in 75/25 acetone/distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 p.s.i. (207 kPa). The insects were transferred from the 8 ounce cup into the cells of the H.I.S. tray (one insect per cell). The trays were covered and held at 27°C and 50% relative humidity for 48 h

after which time readings were taken on the twelve cells with lima bean leaves. The four remaining cells were read 7 days later for delayed toxicity readings. Of the compounds tested, the following gave control efficacy levels of 80% or higher: 3*.

* - tested at 250 ppm.

TEST B

Southern Corn Rootworm

Test units, each consisting of an 8 ounce (230 mL) plastic cup containing a one-inch square (2.54 cm^2) of a wheatgerm diet, were prepared. Solutions of each of the test compounds in 75/25 acetone/distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 p.s.i. (207 kPa). After the spray on the cups had dried, five second-instar larvae of the southern corn rootworm (*Diabrotica undecimpunctata howardi*) were placed into each cup. The cups were then held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. The same units were read again at 8 days. Of the compounds tested, the following gave control efficacy levels of 80% or higher: 1, 3* and 6.

* Test conducted at 250 ppm.

TEST C

Aster Leafhopper

Test units were prepared from a series of 12 ounce (350 mL) cups, each containing oat (*Avena sativa*) seedlings in a 1 inch (2.54 cm) layer of sterilized soil. The test units were sprayed as described in TEST A with individual solutions of the test compounds. After the oats had dried from the spraying, between 10 and 15 adult aster leafhoppers (*Mascrosteles fascifrons*) were aspirated into each of the cups. The cups were covered with vented lids and held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1*, 3*.

* Test conducted at 250 ppm.

TEST D

Two-Spotted Spider Mite

One inch squares (2.54 cm) of kidney bean leaves that had been infested on the undersides with 25 to 30 adult mites (*Tetranychus urticae*) were sprayed with their undersides facing up on a hydraulic sprayer with a solution of the test compound in 75/25 acetone/distilled water solvent. Spraying was accomplished by passing the leaves, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.55 pounds of active ingredient per acre (about 0.5 kg/ha) at 30 p.s.i. (207 kPa). The leaf squares were then placed underside-up on square of wet cotton in a petri dish and the perimeter of the leaf square was tamped down onto the cotton with forceps so that the mites cannot escape onto the untreated leaf surface. The test units were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 5 and 6.

TEST E

Boll Weevil

Test units consisting of 9 ounce (260 mL) cups containing five adult boll weevils (*Anthonomus grandis grandis*) were prepared. The test units were sprayed as described in TEST A with individual solutions of the test compounds. Each cup was covered with a vented lid and held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2*.

* Test conducted at 250 ppm

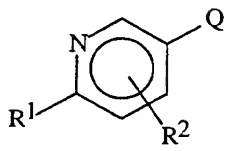
TEST F

Contact Test Against Black Bean Aphid

Individual nasturtium leaves were infested with 10 to 15 aphids (all morphs and growth stages of *Aphis fabae*) and sprayed with their undersides facing up as described in TEST A. The leaves were then set in 3/8 inch (0.94 cm) diameter vials containing 4 mL of sugar solution (approximately 1.4 g per liter) and covered with a clear plastic 1 ounce (29 mL) cup to prevent escape of the aphids that drop from the leaves. The test units were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2*, 3*.

CLAIMS

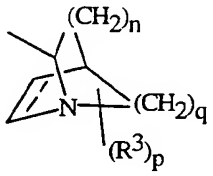
1. A compound of the formula



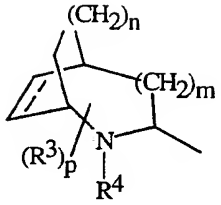
I

wherein:

Q is selected from the group



Q-1



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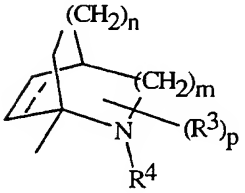
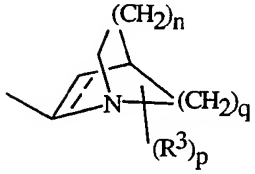


Q-3

and



Q-4

where the broken line represents an optional chemical bond;

R^1 and R^2 are independently selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^5)R^6$, OR^5, $C(O)R^5$, $C(O)OR^5$, $C(O)N(R^5)R^6$, SR^5, $S(O)R^5$, $S(O)_2R^5$, $S(O)_2N(R^5)R^6$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl; R^2 being attached to any unsubstituted aromatic ring carbon; and R^1 and R^2 are not both hydrogen when Q is Q-1 or Q-4, n is 1, R^3 is H and q is 2;

R^3, which is attached to any carbon of the azabicyclic ring including the carbon directly attached to the heterocyclic aromatic ring, is selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^7)R^8$, OR^7, $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7, $S(O)R^7$, $S(O)_2R^7$, $S(O)_2N(R^7)R^8$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^4 is selected from the group H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, $N(R^9)R^{10}$, $C(O)R^9$, $C(O)OR^9$, $C(O)N(R^9)R^{10}$, SR^9, $S(O)R^9$, $S(O)_2R^9$, $S(O)_2N(R^9)R^{10}$, benzyl and $CH(CH_3)Ph$; provided when any of R^1, R^2, R^3 or R^4 is $S(O)R^5$, $S(O)_2R^5$, $S(O)R^7$, $S(O)_2R^7$, $S(O)R^9$, or $S(O)_2R^9$ then R^5, R^7 and R^9 are other than H;

R^5, R^6, R^7,R^8, R^9 and R^{10} are independently selected from the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from W, and benzyl optionally substituted with 1 or 2 substitutents independently selected from W;

W is selected from the group halogen, NO_2, CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

m and n are independently 0, 1 or 2;

p is 1 or 2; and

q is 1, 2 or 3.

2. A compound according to Claim 1 wherein Q is Q-1.

3. A compound according to Claim 2 wherein

R^1 is selected from the group H, halogen and C_1-C_2 alkyl;

R^2 is selected from the group H and Cl;

R^3 is selected from the group H, halogen, C_1-C_6 alkyl and OR^7;

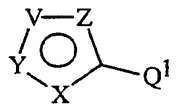
R^5 is selected from the group H and C_1-C_4 alkyl; and

n is 0 or 1.

4. A compound according to Claim 3 which is

7-(6-chloro-3-pyridinyl)-1-azabicyclo[2.2.1]heptane.

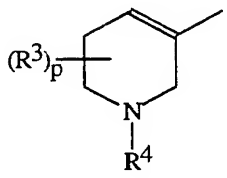
5. A method for controlling arthropods comprising contacting the arthropods or their environment with an arthropodicidally effective amount of a compound of the formula:



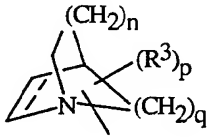
II

wherein:

Q^1 is selected from the group

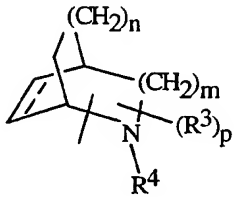


Q-5



Q-6

and



Q-7

;

where the broken line represents an optional chemical bond;

V, X, Y and Z of the ring are each independently selected from the group O, S, N, $-C(R^1)-$, $-C(R^1)=C(R^2)-$, $-C(R^1)=N-$ and $-N(R^{11})-$; provided that (i) no more than one of V, X, Y or Z is $-C(R^1)=C(R^2)-$, $-C(R^1)=N-$, $-N(R^{11})-$, O or S, (ii) at least one of V, X, Y or Z is N, (iii) when the ring is a 5-membered ring containing two N and one O or S, and Q is Q-6, then the ring is attached to the 2-position of Q^1 and (iv) when the ring is a 5-membered ring containing two N and one O or S, then Q is other than Q-5;

R^1 and R^2 are independently selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^5)R^6$, OR^5, $C(O)R^5$, $C(O)OR^5$, $C(O)N(R^5)R^6$, SR^5, $S(O)R^5$, $S(O)_2R^5$, $S(O)_2N(R^5)R^6$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^3, which is attached to any carbon of the azacyclic ring including the carbon directly attached to the heterocyclic aromatic ring, is selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6

haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^7)R^8$, OR^7, $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7, $S(O)R^7$, $S(O)_2R^7$, $S(O)_2N(R^7)R^8$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from the group NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^4 and R^{11} are independently selected from the group H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, $N(R^9)R^{10}$, $C(O)R^9$, $C(O)OR^9$, $C(O)N(R^9)R^{10}$, SR^9, $S(O)R^9$, $S(O)_2R^9$, $S(O)_2N(R^9)R^{10}$, benzyl and $CH(CH_3)Ph$; provided when any of R^1, R^2, R^3 or R^4 is $S(O)R^5$, $S(O)_2R^5$, $S(O)R^7$, $S(O)_2R^7$, $S(O)R^9$, or $S(O)_2R^9$ then R^5, R^7 and R^9 are other than H;

R^5, R^6, R^7,R^8, R^9 and R^{10} are independently selected the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from W, and benzyl optionally substituted with 1 or 2 substitutents independently selected from W;

W is selected from the group halogen, NO_2, CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

m and n are independently 0, 1 or 2;

p is 1 or 2; and

q is 1, 2 or 3.

6. A method according to Claim 5 wherein:

R^1 is selected from the group H, halogen and C_1-C_2 alkyl;

R^2 is selected from the group H and Cl;

R^3 is selected from the group H, halogen, C_1-C_6 alkyl and OR^7;

R^5 is selected from the group H and C_1-C_4 alkyl; and

m and n are independently 0 or 1.

7. A method according to Claim 6 wherein:

V is N;

X is $-C(R^1)=C(R^2)-$;

Y and Z are $-C(R^1)-$; and

Q^1 is Q-6.

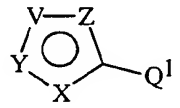
8. A method according to Claim 6 wherein:

V is N;

X is S;
Y and Z are -C(R^1)-; and
Q^1 is Q-6.

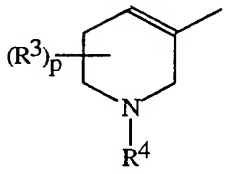
9. A method according to Claim 6 wherein:
the ring contains two N and one O or S; and
Q^1 is Q-6.

10. An arthropodicidal composition comprising a carrier and an arthropodicidally effective amount of a compound of the formula:

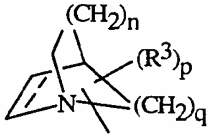


II

wherein:
Q^1 is selected from the group

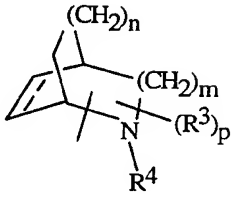


Q-5



Q-6

and



Q-7

where the broken line represents an optional chemical bond;
V, X, Y and Z of the ring are each independently selected from the group O, S, N, -C(R^1)-, -C(R^1)=C(R^2)-, -C(R^1)=N- and -N(R^{11})-; provided that (i) no more than one of V, X, Y or Z is -C(R^1)=C(R^2)-, -C(R^1)=N-, -N(R^{11})-, O or S, (ii) at least one of V, X, Y or Z is N, (iii) when the ring is a 5-membered ring containing two N and one O or S, and Q is Q-6, then the ring is attached to the 2-position of Q^1 and (iv) when the ring is a 5-membered ring containing two N and one O or S, then Q is other than Q-5;
R^1 and R^2 are independently selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2,

$N(R^5)R^6$, OR^5, $C(O)R^5$, $C(O)OR^5$, $C(O)N(R^5)R^6$, SR^5, $S(O)R^5$, $S(O)_2R^5$, $S(O)_2N(R^5)R^6$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^3, which is attached to any carbon of the azacyclic ring including the carbon directly attached to the heterocyclic aromatic ring, is selected from the group H, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_3-C_6 halocycloalkyl, CN, SCN, NO_2, $N(R^7)R^8$, OR^7, $C(O)R^7$, $C(O)OR^7$, $C(O)N(R^7)R^8$, SR^7, $S(O)R^7$, $S(O)_2R^7$, $S(O)_2N(R^7)R^8$ and C_1-C_6 alkyl substituted with 1 or 2 groups independently selected from NO_2, CN, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

R^4 and R^{11} are independently selected from the group H, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, $N(R^9)R^{10}$, $C(O)R^9$, $C(O)OR^9$, $C(O)N(R^9)R^{10}$, SR^9, $S(O)R^9$, $S(O)_2R^9$, $S(O)_2N(R^9)R^{10}$, benzyl and $CH(CH_3)Ph$; provided when any of R^1, R^2, R^3 or R^4 is $S(O)R^5$, $S(O)_2R^5$, $S(O)R^7$, $S(O)_2R^7$, $S(O)R^9$, or $S(O)_2R^9$ then R^5, R^7 and R^9 are other than H;

R^5, R^6, R^7,R^8, R^9 and R^{10} are independently selected the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, phenyl optionally substituted with 1 or 2 substituents independently selected from W, and benzyl optionally substituted with 1 or 2 substitutents independently selected from W;

W is selected from the group halogen, NO_2, CN, C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkylthio, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_4 alkylcarbonyl and C_2-C_4 alkoxycarbonyl;

m and n are independently 0, 1 or 2;

p is 1 or 2; and

q is 1, 2 or 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D487/08 C07D453/06 A01N43/90 A01N43/82 C07D471/08
C07D453/02 //(C07D487/08,209:00,209:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO,A,93 14636 (DOWELANCO) 5 August 1993 cited in the application see claim 1	5
X	CHEMICAL ABSTRACTS, vol. 62, no. 8, 1965, Columbus, Ohio, US; abstract no. 9101c, A.S. SADYKOV ET AL. 'Syntheses based on anabasine. XIX. Synthesis of 7-methylquinuclidine and alpha-(7-methylquinuclidyl)-beta-pyridine' see abstract & ZH. OBSHCH. KHIM. 34(12), 4104-7 (1964)	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 November 1994	17. 11. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Alfaro Faus, I

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08404

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The scope of claim 5 is so broadly formulated that on grounds of Art. 6 of the PCT (conciseness of claims) and of the Guidelines for Examination in the EPO, Part B, Chapt. III, 2.2 (economic reasons) the search has been based on the examples disclosed in the description.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US 94/08404

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9314636	05-08-93	US-A-	5244906	14-09-93
		AU-B-	651516	21-07-94
		AU-B-	3239693	01-09-93
		BR-A-	9205804	17-05-94
		EP-A-	0577788	12-01-94